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TIME AND CHEMICAL CHANGE

The Development of Temporal Concepts in Chemistry
with Special Reference to the Work of Augustus
Vernon Harcourt.

M.Christine King Ph.D. (Manchester)

A thesis submitted to The Open University, for
the degree of Doctor of Philosophy in the History
of Science.

1980

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Tempus et Locus sunt omnium rerum affectiones
communes sine quibus nihil omnino potest
existere.

Time and Place are common affections of all
things without which nothing whatsoever can exist.

Isaac Newton, circa 1692.

HD24 / HD25

MEMORANDUM

The work in this thesis is an account of research carried out by the author during 1976-1979. Except where specifically acknowledged by reference, the content of this thesis has not been previously submitted for another degree of this or any other University or Institute of learning. Section 2.4.3.(d) has previously been published, (New Scientist, 1979, 82, 1110).

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London, June 1980

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ABSTRACT

The concept of time is an important one in the History of Philosophy and of Science. But ideas concerning time and its related phenomenon, that of change, are inherently complex. The study of chemistry involves an understanding of the process of change, a time-dependent function. In fact, the development of temporal ideas in chemistry evolved very late in its theory, around 1850, when Ludwig Wilhelmy first carried out measurements of chemical rate and Alexander Williamson, in the same year, published his ideas on the dynamics of chemistry.

In chemistry, the concept of time is to be found most clearly established in the discipline of reaction kinetics. In its development, this has been bound to the idea of the course of chemical change, as a phenomenon quite distinct from the study of the products of chemical reaction, or chemical composition, on which many of the early chemists were so deeply engrossed. The establishment of time into chemical theory was due largely to the ideas and work of Guldberg and Waage in Norway, and Harcourt and Esson at Oxford.

Harcourt recognised at a very early stage in his studies that what chemists had always neglected was the close observation of the actual course of chemical change, of the time factor involved in these changes. The foundations of these ideas were laid at the very beginning of Harcourt's long career at Oxford, but he was to spend the subsequent fifty years perfecting his techniques.

Perhaps because of the late development of their time awareness, some philosophers of science have come to believe that chemists desired, somehow, to 'eliminate time' from chemical theory. The present work is an attempt to trace the evolution of temporal ideas in chemistry and the eventual recognition of the course of chemical change as a dynamic phenomenon. It also discusses the role of philosophy in the development of chemical theories, a development which is bound, like all events, to the element of time.

Part 1

1.1 Introduction

1.1.1 The Development of Temporal Concepts in Chemistry

It may be said that, since around 1865, when Lewis Carroll first published his Alice tales, the subject of time could not be discussed sensibly without reference to this enigmatic work. All the diverse characteristics which make time such a complex problem to approach, are contained, somewhere, among its pages. The present work is no exception, since it deals with chemistry and the history of chemical change. Like the White Queen in Alice, whose rule was 'jam tomorrow, and jam yesterday, but never jam today', we find the problem of time in chemistry is one of knowing how to recognise the different stages of change. This required, first, the ability to understand the course of chemical phenomenon. In any process of change, there must come, sometime, a stage of 'jam today', which was Alice's objection to the dilemma. This was also the very same problem faced by chemists in measuring a chemical process in the act of changing. In effect, a chemical process, whether it be fast or slow, is a continuous process. The difficulty with comprehending the idea of continuity is that, (as the White Queen put it, 'its jam every other day : today isn't any other day'), it is impossible to know when the actual limits of change are occurring. As Alice said, it can become 'dreadfully confusing.'

This very confusing aspect of time was to pose insurmountable problems for chemists for a long period during the history of chemistry. Initially, chemists had to be content with not so much evolving an understanding of the actual change itself, which relates to the later concept of reaction mechanism, but merely to measuring how fast or slowly the change was occurring. Historically, this step in the development of chemistry took place very late indeed, around 1850, in a discipline whose origins are lost in the distant past. In the process of the present work, it has been gratifying to discover that the links between temporal concepts in chemistry and the logic of Alice, were not entirely imaginary but quite real, in the persons of the chemist Augustus Vernon Harcourt and Alice's creator, Charles Dodgson. Their lives were inter-twined in a very special period of development in both chemistry and literature.

The present thesis attempts to trace how the development and an increasing understanding or involvement of temporal concepts in chemical phenomena have been related to the evolution of chemistry as a scientific discipline. In his Lectures on the Elements of Chemistry Joseph Black wrote,

Chemistry is not yet a science, we are very far from the knowledge of first principles. We should avoid anything that has pretensions of a full system.

This work was published in Edinburgh in 1803. His own studies on heat, one of the major 'imponderables', was to aid, indirectly, the inception of the concept of rates of change in chemical reactions.

In chemistry, the concept of time is now to be found most clearly established in the discipline of reaction kinetics. In its development this concept has been bound to the realisation of the course of chemical change as a phenomenon, quite distinct from the study of material products of a chemical reaction. The innate complexity of the former, a process which could not be directly observed, unlike the investigation of tangible products, is perhaps one explanation as to why its initial realisation, and its subsequent acceptance and utilization, was so late to emerge in the history of chemistry.

The establishment of the rate of chemical change provides an interesting example of the fate of anachronistic scientific ideas. It is now generally accepted that Wilhelmy's work on the hydrolysis of cane sugar in 1850 was the first "exact" chemical rate measurement. Wilhelmy had based his method on familiar physical analogies. This pioneering study, however, was destined to remain unrecognised, until long afterwards when it was rescued by Ostwald from obscurity. In the meantime, the idea of chemical dynamics was to be re-developed from two different fronts.

Around the middle of the nineteenth century, the search for the elusive affinity forces held to be responsible for all chemical phenomena, was, as yet, far from over. In Norway, the chemist Peter Waage and mathematician Cato Maximilian Guldberg began their investigation into reaction rates around 1864. The theory behind their work was based upon ideas of chemical affinity and mass action, long before recognised by Berthollet in his Essai de Statique Chimique, which had been published over half a century previously. Chemically considered, Guldberg and Waage's work was based on a sound substratum, the traditional search for an understanding of the forces of chemical action.

Almost simultaneously, in England, another team also consisting of a chemist, Augustus Vernon Harcourt, and a mathematician, William Esson, began investigations into the course of chemical change. Their approach differed significantly from their Norwegian contemporaries. From the very beginning, their theory was based upon a physical model, and largely ignored the conventional chemical basis of affinity. In this, of course, they had been anticipated by Wilhelmy who had also assumed it reasonable to apply mechanical laws directly to chemical change.

Harcourt and Esson's work firmly established the vital concept of time into chemical change, and in many ways marked a break from the traditional chemical methods of the day. By their style of analysis, in which chemical

affinity was not made the starting point, nor even deemed necessary for consideration. Harcourt and Esson were setting a new tradition which has clearly transmitted to the field of modern chemical dynamics, whose laws were yet to be formulated. This approach was particularly apparent in the later rate studies of J.H. van't Hoff. Harcourt and Esson's work was also distinguished by the complexity of the chemical system upon which they embarked their investigation. The consistent precision of their analytical methods in following the course of the complex changes was to introduce a new level of accuracy into chemical analysis.

Their studies centred initially around the oxidation of oxalic acid by potassium permanganate, in dilute sulphuric acid, in which they varied the proportions of reactants. In order to follow the course of the chemical change, it was imperative to find a means whereby the reaction could be terminated at will. This, Harcourt and Esson achieved by successfully pioneering a new method of quantitative analysis. The addition of excess potassium iodide was capable of stopping the oxidizing action of the permanganate and the liberated iodine was subsequently determined by using a solution of sodium thio sulphate, a method which has been continuously utilized in volumetric analysis since that time.

Their investigations, which were to extend over almost half a century, and their approach to chemical analysis were to establish the study of the course of

chemical change to a new and accepted level. So much so, that later work by others, such as O'Sullivan and Thompson, for instance, was based on the assumption of a universal applicability of Harcourt and Esson's results. O'Sullivan and Thompson's deductions were subsequently to help bring about the final overthrow of the vitalism theory, as we shall see in a later section.

The background to the period which links these two major pioneering contributions by Harcourt and Esson and their Norwegian counter-parts to chemical rate studies provides an interesting picture of chemistry in mid-19th century Europe. Guldberg/Waage and Harcourt/Esson, as we shall see, approached the problem of reaction velocity from different standpoints, although their analysis showed some similarities. The differences must reflect, to no small degree, the somewhat different schools of chemical thought existing at that time in different countries throughout Europe. There is every evidence that Waage's chemical approach to rate problems had its origins in the period he spent in the laboratories of Bunsen in Heidelberg, before returning to his native Norway to commence work with Guldberg. Neither Harcourt nor Esson appear to have spent any portion of their training abroad. Nevertheless, a link to the same laboratories in Heidelberg may have existed through Harcourt's University mentor Benjamin Brodie, who had been Bunsen's pupil before going to Oxford.

The rate studies of Guldberg and Waage, Harcourt and Esson, followed some fifteen years after the work of Ludwig Wilhelmy. Yet there is no indication that either team was aware of Wilhelmy's work, nor indeed that they were aware of the existence of each other during the early years of their respective experiments.

The development of chemical kinetics was based upon the recognition of chemical processes as comprising dynamic rather than static states. In the same period in which Wilhelmy began to quantify the laws of chemical change, the chemist Alexander Williamson was advocating the idea of dynamic chemistry. Williamson considered that what was needed in order to bring about the transition from the traditional static picture of chemistry to that of a dynamic point of view was the introduction of the time factor into chemical thought.

The concept of time in chemistry has remained elusive throughout the long history of chemical development. That the time factor is involved in every chemical change is not a profound discovery. What is interesting is the attitude of those concerned with chemical phenomena towards the element of time. The problems and difficulties of understanding this enigmatic concept were not peculiar to chemists alone, as we shall see in the brief introduction to the concepts of time. They were common to every school of thought in many civilizations and in every age of development. What does appear to distinguish the history of chemical progress from that of the other major physical sciences is that no philosophy relating to time has emerged

in any form. The evidence for this is so overwhelming that more than one philosopher of science has suggested that chemists sought, for some reason as yet unexplained, to eliminate the time factor from their theories.

The reasons for such a historical development are necessarily related to the origins and to the meaning of chemistry, its laws and its theories and, above all, to the evolution of an idea: the idea that chemical change occupies Time and Place, which in Newton's words are "common affections of all things, without which nothing whatsoever can exist." ¹

1.1.2 The Conceptual Basis of Time

The concept of time is an essential one in the development of knowledge and has been the subject of much thought, discussion and dialogue throughout history. In many respects, it bears a close relationship to other fundamental concepts such as space and the origin of the Universe, and very frequently, time has taken on spiritual significance. By the very diversity of its nature, the study of time has become part of an extremely broad and complex spectrum of interdisciplinary subjects. In both science and philosophy, the subject of time has occupied a very special central role within the history of ideas and the development of universal knowledge.

1. See this work, p. 27

1.1.2 Continued

It would be difficult, if not totally futile, to attempt a general introduction to the meaning of time in the present work. As the quantity of extant literature shows, few subjects have been pondered so much, so frequently and by so many as the nature of time.¹ The origins of modern physics and chemistry alike are to be found rooted in the inherited teachings of Greek antiquity. It is of relevance therefore, to look briefly at the philosophy of western scientific thoughts from which were formed the conceptual basis of temporal ideas important to the development of the sciences.

The paradoxical nature of time as epitomising both change and changelessness was expressed by Plato in Timaeus when he set the place of time in the creation of the Universe as 'the moving Image of Eternity'.²

But in science, it is with Aristotle that many of the later attributes of time have become permanently associated. The statement generally associated with Aristotle, that 'time measures motion' is, however, not strictly accurate; he believed that time was something in the phenomenon of

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1. A brief bibliography on time and philosophy is included at the end of this section.
 2. See J.F. Callahan, Four Views of Time in Ancient Philosophy, Harvard University Press, 1948, Chap.1.

1 .1.2 Continued

motion. Originally, his study of motion led him to the definition of time as 'the number of change in respect of before and after', a meaning perhaps closer to our modern view of time than is usually credited to him.¹ Aristotle conceived time as being universal, continuous and uniform, flowing from past to future. The present, or now, has no dimension since it merely marks a transition of the future into the past, and a continuum cannot consist of points. For Aristotle, time and change (or motion) were mutually dependent.

The extent to which the teaching of Aristotle and the early Greek Schools had become the very quintessence of mid-millennium European thoughts can be gauged by the seriousness, intensity, indeed viciousness of attacks with which later scholars thought fit to subject them.. History shows that posterity was not entirely grateful to the thoughts of the great Schoolmen; many felt that before true knowledge could be obtained and reason, and science, triumph, the old teachings had first to be rejected,

1. The Works of Aristotle, Ed. by W.D. Ross, Oxford, 1930, Vol.2. Physica, translated by R.P. Hardie, R.K. Gaye. For a discussion on Aristotle's temporal ideas, see: H. Weiss, Notes on the Greek Ideas referred to in Van Helmont's De Tempore, Osiris, 1948, 8, 418; Isis, 1942, 33, 624.

1.1.2 Continued

preferably annihilated.¹ In the 17th century, Francis Bacon devoted The Masculine Birth of Time² to the total rejection of scholastism. To Bacon the false philosophy of the Greeks was the great obstacle to a divinely promised revolution in human affairs. In the strongest possible words, Bacon wrote:

This kind of degenerate learning did chiefly reign among the Schoolmen; who, having sharp and strong wits, and abundance of leisure, a small variety of reading (their wits being shut up in the cells of a few authors, chiefly Aristotle their Dictator, as their persons were shut up in the cells of monasteries and colleges),

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1. On Renaissance criticisms of Aristotle's theory of Time, see P.E. Ariotti, Toward Absolute Time: the Undermining and Refutation of the Aristotelian Conception of Time in the 16th and 17th Centuries, Annals of Sci., 1973, 30, 31-50; S. Hutton, "Some Renaissance Critiques of Aristotle's Theory of Time", Ann. of Sci. 1977, 34, 345.
 2. B. Farrington, Temporis Partus Masculus; an untranslated Writing of Francis Bacon, Centaurus, 1951, 1, 193; ibid, Francis Bacon; Philosopher of Industrial Science, New York, 1949, contains an account of Bacon's strong opposition to Aristotle's teaching.

1.1.2. Continued

and knowing little history, either
of Nature or Time, did, out of no
great quantity of matter, and infinite
agitation of wit, spin out unto us
those laborious webs of learning
which are extant in their books.¹

Bacon believed that his generation of thinkers were in
danger of forgetting the most fundamentally important
factor known to humanity, the divine Creator and His work,
Nature. He vehemently attacked the habit of the Schoolmen,
and their posterity, of wishing to be like gods, and

we, their posterity, still more so.
We create worlds. We prescribe laws
to Nature and lord it over her.
We want to have all things as suits
our fatuity, not as fits the divine
wisdom, not as they are found in
Nature. We impose the seal of our
image on the creatures and work of
God, we do not diligently seek to
discover the seal of God on things.

1. F. Bacon, The Advancement of Learning, 1605; see
B. Willey, The 17th Century Background, London, 1940;
see also J.R. Partington, A History of Chemistry,
London, 1961, Vol.2, 389.

1.1.2. Continued

Therefore not undeservedly have we
fallen from our dominion over the
Creation.¹

Bacon's eloquent disquisitions provide us with a lively picture of the intellectual climate of his day, of the conflicts between scientific rationalism and alchemical mysticism. As a philosopher, Francis Bacon stands poised between the new age of learning of the 17th and 18th centuries and the rigid Aristotelian pedagogy which dominated the Middle Ages. Together with a few other notables of his time (Bruno, Gilbert, Digby and Thomas Brown for instance), Bacon's ambition for instauration became the mechanism for a new learning. His keen interest in the chemistry (and alchemy) of his day was doubtlessly influenced by the writings of Paracelsus, Hollandus, Croll, Agricola and Valentine for "if Bacon wished to know anything significant about chemistry he would have to go to the experts, the contemporary alchemists, which he did."²

In the evolution of 16th and 17th century chemical ideas, the teachings of Paracelsus and his disciple J.B.van Helmont hold very special places. It is generally recognised

1. F. Bacon, The Advancement, op.cit.

2. J.R. Partington, op.cit, Vol.2, 393.

1.1.2. Continued

that the history of chemistry owes much to the practices of alchemy. What is far more complex to determine is when the transformation of chemistry from a mystical art to its acceptance as a distinct science, took place and how it did so. As Needham has put it,

the great difficulty about change is that it is so hard to know when the limits of one category have been overpassed and the next category entered. Such insensible transitions have therefore always been the thorn in the flesh of formal logic, as we can see by comparing the flexibility of 17th century science with the rigid Aristotelian formalism of the Middle Ages from which it had successfully struggled to free itself.¹

The relationship between the concept of change and chemical processes, both scientifically and historically, is of special interest in the present work and will be discussed again later. Certainly, the Paracelsian influence in the transformation is undisputed. For his role in bringing

1. J. Needham, Science and Civilization in China, Cambridge University Press, 1956, Vol.2, p.76; On time and change in East and West see J. Needham; Time, the Refreshing River, London, 1942; Time and Eastern Man in The Grand Titration, London, 1969

1.1.2. Continued

about reform in the medical, chemical and biological traditions of his day, posterity has honoured this iconoclast with much study.¹ His didactic and revolutionary methods emphasised both the importance of chemistry to medicine and the necessity of conducting experiments by personal observations. This heuristic philosophy was to have paramount influence on his followers.

The turbulent life of Paracelsus and the controversial nature of his ideas have provided an interesting picture of both mysticism and realism in the process of change.² His views philosophy, biology and medicine were based upon analogies between universal macrocosm and microcosm. Time, to Paracelsus, was a phenomenon whose properties were derived from the celestial bodies. The season in which a disease occurred determined its nature; time and Nature provided the cure by making available the correct sequence in which

1. See the 7-pages of bibliography in ISIS, Cumulative Bibliography, London, Ed. by M. Whitrow, 1971-76, p.270-276. Also; H.M. Pachter, Paracelsus: magic into science, New York, 1951. W. Pagel, Paracelsus. An introduction to philosophical medicine in the era of Renaissance, Basel/New York, 1958; T.L. Davis, "Boerhaave's account of Paracelsus and van Helmont, J. Chern, Ed. 1928, 5, 671-81; T.P. Sherlock, "The Chemical Work of Paracelsus", Ambix, 1948, 3, 33-63, 671.

2. See reference 1 above.

1.1.2. Continued

plants made their appearances. Time brought forth flowers in the same way it caused diseases.¹ To Paracelsus, time, synonymous with celestial movements, was the dictator of events, of sickness, and of life and death. This was the parallelism between macrocosm and microcosm, 'the Heaven in Man'. The new medicine advocated by Paracelsus trusted in the interdependence, and the unfailing certainty of astronomical time.

Paracelsus' life spanned the first half of the 16th century. J. Baptist van Helmont succeeded him in the second half, in the years 1577-1644. Discoverer of the concept of gas, the founder of pneumatic chemistry, "forerunner of Boyle and Lavoisier, pioneer of the chemistry of life", van Helmont initiated experiments on fermentation and brought quantified chemistry one step closer by using the balance as an essential part of experiments.² The essence of his philosophy on time have come to us in the work De Tempore, published in 1648.³ Pagel has devoted

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1. W. Pagel, J. Baptist van Helmont: De Tempore and the history of the biological concept of time. Isis, 1942, 33, 621.
 2. J.R. Partington, "J.B. van Helmont", Ann. Sci, 1936, 1, 359; W. Pagel, "J.B. van Helmont, De Tempore and biological time", Osiris, 1948, 8, 346-417; see also the large number of references in ISIS, Cumulative Bibliography, op.cit.
 3. See W. Pagel, "J.B. van Helmont, De Tempore and biological time", Osiris, 1948, 8, 346-417.

1.1.2 Continued

much scholarship to making the knowledge of this enigmatic personality and his elaborate discourse available and comprehensible.¹ As Pagel pointed out, this one work embodies van Helmont's philosophical, scientific (medical, chemical, biological) and religious convictions, knowledge without dichotomy. Almost as forcible as the actual contents of the work itself, the history of scientific thought as conceived in 17th century Renaissance Europe and, by contrast, the developments of subsequent centuries, appear in these pages with startling clarity. We see ^{how} new contemporary science belies "the unity once formed by the 'Philosophia Naturalis'", wrote Pagel, "(and) split up into a number of independent branches, (taking) the place of a universal science covering all aspects in Philosophy and Nature."² In the history of Renaissance thought, van Helmont emerges as an outstanding 17th century figure, anti-scholastic in the tradition already described,

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1. See W. Pagel: "The religious and philosophical aspects of van Helmont's science and medicine", Suppl. to Bull. Hist. Med, 2, Baltimore, the Johns Hopkins Press, 1944; "van Helmont; 300th anniversary of his death", Brit. Med. J.; 1945, 1, 59; "The reaction to Aristotle in 17th century biological thought; Campanella, van Helmont etc;" Science, Medicine and History. Essays in honour of Charles Singer, Oxford University Press, 1953.
 2. Pagel, ref. 1 , 347.

1.1.2 Continued

a creator of what Pagel describes as 'religious empiricism'. For van Helmont, 'Research is divine service, worship of God', and the object of science to find new methods of alleviation of human suffering.¹ And science was the manifestation of divine service and truth. Like his mentor, Paracelsus, van Helmont advocated the importance of experimentation. As a 'chemist', van Helmont has been said to represent the transition from alchemy to chemistry.²

De Tempore not only contains van Helmont's view of time, but also his total deprecation of peripatetic teaching, which is as vehement as Bacon's. He wrote:

Aristotle was utterly ignorant of the principles of Nature and poor in his knowledge of physics. Therefore he has ridiculously described time, locality, vacuum, infinity, chance and similar abstract concepts, absolutely alien to the realm of nature, as if they were physical objects.³

1. Pagel, op.cit., 347.

2. Jan Baptist van Helmont in H.M. Leicester, H.S. Klickstein, A Source Book in Chemistry 1400-1900, New York, 1952, 23.

3. Pagel, Op.cit., De Tempore, 357.

To van Helmont, time was eternal duration, and to eternity there could be no succession.

"Time cannot be separated from eternal duration...even if there is no body or motion, still time, locality, relations in position, and distance remain the same as they are now...in a similar way I hold Time bound up with no locality, no body and finally no motion, but an entity separate from them. I therefore do not beg time from the circular movement of heaven, the first mobile. For although the motion of heaven takes place in a certain locality, as if it were a certain measure of it, the locality is not identical with the motion, although it takes place in it - in the same way motion is not time, although it takes place in it. Nor can time be generated by motion....¹

1. Pagel, op.cit., 358.

1.1.2 Continued

These ideas stand in marked contrast to the peripatetic dogma of time and motion which had held sway for so long.

Indeed, van Helmont continues,

...year, day, month and nights are not time, but measuring units and accidents of what happens in time, completely alien to and outside time. Thus, naturally, what to us is day, is night to another. Meanwhile, everywhere time is the same, all over the world. Spring, summer, autumn, winter are not time; but alterations of the air, appointed for the change of things in vicissitude.¹

Van Helmont's strong denial of the mathematical nature of time is of special interest in the present work, for the association of time as an integral part of physics, totally divorced from chemical phenomena, appears frequently in the history of temporal ideas. In van Helmont's view,

1. Pagel, op.cit., 358.

it emerges of necessity from their (the Schoolmens) suppositions that each part of time is not one of time, but some mathematical point, indivisible and therefore without duration, outside and remote from time; so(that)also time would consist of indivisible parts... these, however, would not be really indivisible atoms or points of duration, if, by their connection, they were to form something divisible. They are not aware that something indivisible and negative can never grow by connection into something present, actual, long, short, big or small.¹

The establishment of quantification in science has, first of all, required the recognition of mathematical laws as a means of reproducibility. For chemistry, the evolution of this step of development was to take several centuries beyond van Helmont's life-time, as we shall see. But in the 17th century, his criticisms of Aristotelian methods also extended to the denial of the validity of mathematical time in physics,

1. Pagel, op.cit., 359

1.1.2 Continued

Indeed they have...far too much
addicted themselves to Mathematics
while they believed themselves to
be in the field of Nature.¹

To van Helmont then, mathematics or pure numbers, was not compatible with the study of nature, the ultimate goal of science. In his view, the Schoolmen had committed a fatal error in their philosophy of time, for,

they have envisaged a long and short
time, thus reducing time to a quantity.²

Van Helmont's vision of time is conceivably spiritual in origin, a divine entity;

"I therefore believe that true
time is pure,.....is everywhere
and always immutable and in no
way successive...Time is what

1. Pagel, op.cit., 359

2. ibid.

1.1.1 Continued

it is whether motions or changes
occur or not.¹

Van Helmont's philosophy of time in De Tempore is a preamble to his theory on biological time, as shown in his opening sentence - that before discussing longevity, it was desirable to propose a treatise on Time, since long life is inseparably connected with duration. Life, however, could not be measured by time, because its duration was counted by days and years, which, to van Helmont, did not signify time. Although in his perusal of biological and medical knowledge, chemistry became an indispensable part of his philosophy, its role appears to have been, to van Helmont,

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1. Pagel, op.cit, De Tempore, p.365-366. van Helmont also gives an account of how he arrived at his concept of independent time, a biblical genesis. See Pagel. p.363. The paradox presented by an analysis of the conception or origins of time has been dwelt upon by all temporal philosophers, most notably Augustine of Hippo. St. Augustine's questions about time partially resolves the problem by stating what time is not, that is, it is not the motion of the heavenly bodies. More specifically, "I measure the motion of a body by time, but time itself I do not measure. But, truly, could I measure the motion of a body - how long it takes, how long it is in motion from this place to that - unless I could measure the time in which it is moving?" See Problems of Space and Time, Ed. by J.J.C. Smart, New York and London, 1968.

1.1.2 Continued

that of matter "spiritualized."¹ Pagel believes that van Helmont occupies a role in the continuity of the early history of chemistry.² But in van Helmont's De Tempore, the role of time in chemistry itself, as distinct from its part in biological issues, remains a topic untouched. The fact that, for a chemical reaction to achieve its natural conclusion, a time factor was involved, just as much as in biological and pathological processes, was not taken into account; a specifically chemical philosophy of time cannot be found amongst van Helmont's thoughts.

The points of similarity between the temporal philosophy of van Helmont, and that of Newton, and of his mentor Isaac Barrow, have been discussed not infrequently.³ Newton's

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1. Pagel, op.cit.
 2. W. Pagel, "The Spectre of van Helmont and the Idea of Continuity in the History of Chemistry": Changing Perspectives in the History of Science, Essays in honour of Joseph Needham, Ed. M. Teich, R. Young, London, 1973, 100.
 3. See E.A. Burtt, Metaphysical Foundations of Modern Science, New York, 1925 ; P. Ariotti, The Evolution of the Concept of Time in Science in the 16th and 17th centuries, Ph.D. thesis, 1966, University of Melbourne, 254.

influence on subsequent developments in both physics and chemistry has been the subject of much study.¹ Newtonian ideas on time and space were to dominate the sciences from the 18th century without challenge until the present century:

I do not define Time, Space, Place and Motion, as being well known to all. Only I must observe, that the vulgar conceive those quantities under no other notions but from the relation they bear to sensible objects....Absolute, true, and mathematical time, of itself, and from its own nature flows equably without regard to anything external, and by another name is called duration.

And in contrast,

relative, apparent and common time, is some sensible and external (whether accurate or unequable) measure of

1. For an introduction to the concepts of Newtonian chemistry see A. Thackray, Atoms and Powers, Camb. Mass, 1970

T. Levere, Affinity and Matter, Oxford, 1971.

duration by the means of motion, which is used instead of true time; such as an hour, a day, a month, a year ... It may be, that there is no such thing as an equable motion, whereby time may be accurately measured. All motions may be accelerated and retarded, but the true, or equable, progress of absolute time is liable to no change. The necessity of which equation, for determining the times of a phenomena, is evinced as well from the experiments of the pendulum clock, as by the eclipses of the satellites of Jupiter.¹

Although not seriously challenged, criticisms of 'Newton's vision of absolute space and time were to form part of the intellectual milieu of western philosophy in the centuries that followed, created notably by the arguments of Berkeley and Leibniz. It is of interest to note that Faraday's philosophy of time has been traced, not to Newton, but to Berkeley.²

1. Sir I. Newton, Philosophia naturalis, principia mathematica, trans. by A Motte in F. Cajori, Sir Isaac Newton's Principia, Berkeley, 1947.

2. See present work, 337

1.1.2 Continued

Like van Helmont before him, Newton asserted that true time was a divine entity. His Creator was present in absolute space and absolute time, a religious experience in which scientific empiricism had no role.¹ The importance of the concepts of time and space in Newton's philosophy cannot be questioned, problems to which he devoted much of his work.

Time and Place are common affections
of all things, without which nothing
whatsoever can exist.

he wrote.²

Neither was the complexity and philosophical perplexity of those problems denied by Newton,

Still, I admit that an infinite number
of things is difficult to conceive,
and is therefore taken by many people
as impossible: but there are many things
concerning numbers and magnitudes which
to men not learned in mathematics will
appear paradoxical, and yet are entirely
true.....that two neighbouring bodies are

1. F. Cajori, op,cit., 545.

2. J.E. McGuire, "Newton on Place, Time, and God: An Un-published Source", Brit. J. for Hist. of Sci., Vol.II, 38, 1978, 114.

1.1.2 Continued

always able to approach one another
and yet never touch each other; that
motion in a merely finite space can be
increased to infinity; that a point
by moving according to a given law in
a finite time, can go off to infinity,
and conversely can return to us from
infinity in the same time; that a finite
line can be divided at points infinite
in number; and that units successively
added can in finite time become infinite
in number.¹

We are left with no reasonable doubt that Newton intended his
ultimate concept of time and space to relate to a Divine Entity.
As to the true meaning of time, Newton, like all before him,
had to admit a certain sense of the enigmatic, for he concluded
that,

What God did before the creation of this
visible world and outside its (bounds)
is hidden from us and concerning things
unknown nothing is rashly to be affirmed
or denied.²

1. J.E. McGuire, op.cit.

2. J.E. McGuire, op.cit., 121

1.1.2 Continued

Even so great a mind as that of Newton's had to cede the subject of time to the sanctions of the mystical, since

The human race is prone to mystery, and holds nothing quite so holy and perfect as what cannot be understood. Yet in the conception of God this is dangerous, and conduces to the rejection of his existence.¹

There is thus an interesting continuity of thought in the temporal philosophy of Newton and van Helmont, both in their concepts of duration and the ultimate inseparability of God and time. In the Renaissance period and its aftermath, the concept of time had deviated markedly and irrevocably from the philosophy of the Schoolmen, forming a new structure in which van Helmont and Newton appear as chief architects. But in the subsequent development of the physical sciences, the role of time was to take on very different significance for chemistry and for physics.

1. J.E. McGuire, op.cit., 121.

1.1.3 Time and Chemical Thought

In this present work, the most pertinent question to which an answer may be hoped for is perhaps not what time means, even in a chemical context, but what role it played in the development of chemistry. The special aspect of time with which we are concerned in chemistry and its most notable characteristic is its dynamic nature. This alone distinguishes it from all other commonly measurable quantities, such as size, mass, pressure or temperature. Time alone cannot be held constant to allow for the formulation of scientific laws. In real experience, it continuously progresses and changes. In essence, this is the same conclusion as that engendered in the philosophical polemics on time we have already considered, but without dwelling upon its origins.

The evolution of ideas and methods by which this change in time could be incorporated into scientific observations is a part of the history of our understanding of time. To distinguish between different classes of events which are related to time has necessitated the introduction of many temporal terms. In the language of time, a distinction is drawn between time as epoch (i.e. time as measured on a time axis, traditionally regarded in western culture as an infinite, uniform, linear progression, giving time an "arrow" or direction) and interval time which is concerned

1.1.3 Continued

with merely measuring time interludes.¹ In chemistry this may be the measurement of the instant when an event, such as an experiment, is stopped. It is, however, quite obvious that time has not stopped, though the experimenter may choose to stop the time of reaction.²

Chemical changes must, by definition, involve time. This element of time is embodied in chemistry primarily in the related ideas of continuity and rates of change in or between the solid, liquid and gaseous states of matter. In the development of chemistry, from the time of Lavoisier onwards, the overwhelming predilection of chemists was undeniably the pursuit of ever new chemical compounds and compositions rather than for an understanding of the path of chemical change. Knowledge of the fundamental nature of matter is, of course, a necessary precursor to many scientific theories. It may have been thought that once an understanding of chemical composition was achieved,

1. For general ideas on time and its measurement see articles by M. Čapek, G.J. Whitrow in Dic. of Scientific Ideas, P.P. Wiener, (Ed.), 1973-74, New York, Vol. 4, 389, 398.

2. This particular phenomenon of time will be discussed later in connection with Ostwald's statement that chemical equilibrium was a state "independent of time", whilst, at the same time, existing as a dynamic, not a static state.

1.1.3 Continued

comprehension of the nature of chemical change would not be long in following. The history of chemistry shows that this does not appear to have been the case.

The evolution of the theory of chemical atoms has deservedly been the subject of numerous studies. Its discovery and validity was a matter for debate amongst chemists and physicists, a fundamental problem which remained partially unresolved until the end of the 19th century, if not later. As one contemporary writer has put it:

Chemists welcomed the convenience of the theory (i.e. Atomic Theory), as a summary of known facts and employed its language, but they were not prepared to discuss the question of ultimate divisibility of matter. It was sufficient to know that certain masses were undivided by the powers of chemistry.¹

1. D. C. Goodman in C. C. Gillespie, (Ed.), Dictionary of Scientific Biography, Vol. 2, (1970), New York, 484.

1.1.3 Continued

It is tempting to conjecture that had the 19th century chemists been able to resolve their conflicts on matter theory and the atoms, a philosophy of time and space would have emerged for chemistry as it was to do for physics.¹ However, as we said earlier, subsequent developments of chemistry veered strongly towards the creation of ever-increasing new material products, and away from causality. The Oxford chemist Augustus Vernon Harcourt, whose work is of special interest in the present study, wrote in 1875:

we are occupied in amassing a vast collection of receipts for the preparation of different substances, and facts as to their composition and properties, which may be of no more service to the generalizations of the science, whenever our Newton arises, than were, I conceive, the bulk of the stars to the conception of gravitation.²

1. On chemical atoms and space, see Foundations of Stereochemistry, Memoires by Pasteur, van't Hoff, Le Bel and Wislicenus, trans. by G.M. Richardson, New York, 1901.

2. B.A. Reports (Chem. Section), 1875, 32-36.

1.1.3 Continued

Harcourt pleaded with chemists of his day that,

our aim is to discover the laws which govern the transformation of matter.¹

But underlying the problems of establishing general laws of chemistry were deep epistemological differences as to what knowledge of chemistry really was. The open debates on the nature of atoms and the discreteness or continuity of chemical processes appear to have been confined to the arguments of only a few chemists.² In the evolution of science however, general patterns of such thoughts may be distinguishable at different stages of development. As Pledge wrote,

In general, possession of the mind by continuity is natural when great new syntheses are waiting to be made, its possession by the discrete when it becomes necessary to examine the

1. B.A. Reports (chem.Sec.), 1875, 32-36.

2. The atomic debates in chemistry will be discussed in a later section. The philosophical problem of continuity and discreteness in chemical processes appears to have occupied few chemists' thoughts. One of the few was Edmund Mills.

1.1.3 Continued

last great synthesis to see what it has really accomplished and why insuperable difficulties confront it.¹

The development of chemistry has a difficult and complex history, and in many ways remains far less understood today than the history of many other sciences.² The problems presented by an understanding of time and its related concepts such as continuity (as embodied in chemical equilibrium for example) are common to both chemical and physical sciences, as historians of science have recognised,

continuity is one of the most abstract and difficult of ideas. One or two similar ones, such as cause and effect and epigenesis have always teased the human mind, acting always as an irritant and spurring common sense, in the end,

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1. H.T. Pledge, Science since 1500, London, 1939, reprinted 1966, 324.
 2. ibid., 326.

1.1.3 Continued

to turn away from them and to venture,
rather than be hypnotised by insoluble
problems on the long road to science.¹

This "common sense" approach to the paradoxes and dilemma of time, and the related concepts of change and continuity, may aptly describe the reactions of chemists in the 18th and 19th centuries. For whereas the history of temporal concepts in the development of physics and the biological sciences has been well documented, up to and including the contemporary era, this does not appear to be true in the case of chemistry.²

And yet, as Farber has pointed out, the practical importance of time studies should have become evident in connection with the growing size of chemical manufactures

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1. H.T. Pledge, op.cit., p.324. On the development of ideas of continuity see S. Bachner, "Continuity and Discontinuity in Nature and Knowledge", Dic. of Scientific Ideas, P.P. Wiener, (Ed.), Vol. 4, New York, 1973-74, 492.
 2. It is an interesting fact that in a recent bibliography on time, containing 3005 entries there is only one entry under chemistry and this refers to chemical evolution and the origin of life; see Time, a Bibliography, compiled by E.S. Krudy, T. Bacon, R. Turner, Washington, 1976.

1.1.2 Continued

from at least the beginning of the 19th century.¹ In a tantalising sentence Farber seems to hint that there is an underlying "psychological factor" as to why chemists were late in developing time-consciousness.² Unfortunately, he does not elaborate upon this theme. Perhaps Farber was referring to the tendency of chemists to "eliminate" time from their subject, a habit which has been noted by several authors, as will emerge in the present work.

1. E. Farber, "Early Studies Concerning Time in Chemical Reactions", Chymia, 1961, 7, 135; in an exhaustive search on the subject of time in chemistry, the only other source on the topic to have emerged is O.T. Benfey, "Concepts of Time in Chemistry", J. Chem. Ed., 1963, Vol. 40, 11, p. 574., which deals with time in thermodynamics and the role of stereo-chemistry, kinetics and mechanisms in chemical education.
2. Farber, ibid.

The understanding of what constitutes chemistry, and more especially, chemical change, forms a vital link in the evolution of temporal theories in chemical studies.¹ The development of time concepts in chemistry evolved only after the actual process of chemical change had been recognised as a distinct phenomenon, quite separate from the mere fact that some change of matter had occurred. This recognition forms a central part of how chemistry was practised throughout the different ages. Chemists, seeking to make their discipline more clearly defined, had first of all to create a language, one with a very specific meaning. It is of relevance, therefore, to look at the different meanings given to chemistry and its method at different times in its development; and particularly at the threads of similarities linking these definitions, which were separated by both time and distance.

"The purpose of chemistry seems to have changed much from time to time", wrote Pattison Muir at the turn of the present century,²

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1. The meaning of the word chemistry is traditionally assumed to have evolved from early alchemy. Rodwell, writing in 1874, considered the true derivative of the word to be Coptic, khems or chems, signifying obscure, occult and connected with the Arabic chema, to hide; G.F. Rodwell, The Birth of Chemistry, London, 1874.
 2. M.M. Pattison Muir, A History of Chemical Theories and Laws, London, 1907, vii.

1.2 Continued

At one time, chemistry might have been called a theory of life, and at another time a department of metallurgy; at one time a study of combustion, and at another time an aid to medicine, at one time an attempt to define a single word, the word element and at another time the quest of the unchanging basis of all phenomena. Chemistry has appeared to be sometimes a handicraft, sometimes a philosophy, sometimes a mystery, and sometimes a science.¹

This picture of chemical evolution implies that the notion of chemistry was, and had always been, open to interpretation. Any single one of the named characteristics which united the divers phenomena, all of which were interdependent, could claim to be chemical in nature.

Indeed, even a brief perusal of early chemical literature shows that the origins of chemistry lie deeply embedded in a labyrinth of different, though related, concepts. What is equally evident, is that this lack of clarity in definition was of deep concern to chemists from

1. M.M. Pattison Muir, op.cit.

1.2 Continued

an early stage. In the 8th century for instance, Geber considered chemistry as that branch of natural science which investigates 'the properties and generation of minerals and of substances obtained from animals and plants.'¹ Furthermore it embraced the study of all Nature's domain, for 'how can a man imitate a thing of which he knows nothing?'²

Amongst those who searched successfully for a new meaning of chemistry at the end of the 16th century was Andreas Libavius, who has been credited with the invention of chemistry as a discipline.³ Like van Helmont, who battled against the teachings of the Schoolmen, Libavius sought to

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1. The Works of Geber, trans. by R. Russell, 1678, a new edition, with introduction by E.J. Holmyard, London and Toronto, 1928; see also E.J. Holmyard, Chemistry to the Time of Dalton, Oxford, 1925, p.16.
 2. The rules set out by Geber, intended for those practising chemistry, appear in the light of later didactic works, surprisingly modern. Thus, the operator should know the reason for performing each operation; the instructions must be properly understood; the impossible and profitless, should be avoided; he must not be deceived by appearances into bringing his operations to too hasty a conclusion. But in keeping with the thinking of the day, Geber also considered that when practising the art of chemistry, time and the season had to be carefully chosen, to be in harmony with Nature; Holmyard op.cit.
 3. O. Hannaway, The Chemists and the Word, Johns Hopkins Univ. Press, 1975.

break old traditions using the persuasion of methodology. His battle was against the alchemical ideology of the Paracelsians and his aim, to replace it by a text-book tradition of chemistry, a tradition which was to be of critical influence on the development of the subject in subsequent centuries.¹

Libavius' task was to analyse the diverse alchemical prescriptions and methods of operation, and, by methodology and logic, to organise these into a comprehensive 'art'. Chemical art was concerned with extraction, mixing and separation and above all with change and transmutation, of matter, forms and colours. For Libavius, contrary to the chemical traditions of the day, smelting of metals and the activities of the pharmacist did not belong to the domains of chemistry.² True chemistry required a new and independent formalism.

The problems encountered in making chemistry a 'methodized didactic' included the question of terminology in common usage at the time. Libavius' goal was to define chemistry, 'for it consists of homogeneous precepts set out

1. O. Hannaway, op.cit., 153.

2. ibid., 123

1.2 Continued

in methodical form and order'.¹ The complexities and diversities of the art of chemistry however, made this logical and vitally necessary step extremely elusive. The results of his labours have come down to us in the form of the Alchemia, published in 1597, at Frankfort, and described as an encyclopedia of the operations and recipies of which chemical art was then comprised. But the significance of this achievement was far greater than that of a mere addition to alchemical literature. In Hannaway's words,

this work is the first text
which conceives of chemistry
as an independent and integral
discipline, divorced from its
applications and which seeks
to organise the techniques and
prescriptions of the subject in
such a way that they can be
taught. It marks the appearance
of a new scholarly discipline on
the intellectual horizon - the
discipline of chemistry.²

1. O. Hannaway, op.cit., 124.

2. O. Hannaway, op.cit., 143

The need for this articulation of the subject, a closer examination of chemical cause and effects, and, ultimately, an ability to stipulate its laws, was indeed a necessary pre-cursor to the later quantification required to make chemistry an 'exact' science. Only by questioning and distinguishing between true chemistry and what was now seen as the highly suspect, if not outright fraudulent, practices of alchemy, was it possible to set the stage for another era in the history of chemistry. In the 17th century, this 'noble art' still included the traditional metallurgy, pharmacology, medicine and indeed physiology since all were vital components of Nature. Their understanding was considered to be of indisputable importance to chemistry. Indeed, Christopher Glaser wrote in 1663,

They that have any true knowledge of this noble art, are without a doubt, fully persuaded of the usefulness of it; for it is the key which alone can unlock to all naturalists the door of Nature's secrets; by reducing things to their first principles; by giving them new forms; and by imitating

Nature in all its productions and physical alterations.¹

The function of chemistry, to Glaser, was

to separate (them), purify each by itself, then unite them again, to make of them bodies much purer, and more active than they were before.²

Glaser's words were not atypical of views on the purpose of chemistry in 17th century Europe.

For chemistry, however, it is the 18th century which stands as something of a water-shed, the era which was rewarded with the work of Lavoisier; a century in which 'chemistry began to take shape as a definite branch of

1. Christopher Glaser, Traité de la Chymie, Paris, 1663; Trans. anonymously as The Compleat Chymist or A New Treatise of Chymistry, London, 1677. Reproduced in part in : Nature and Nature's Laws, Ed. by M. Boas Hall, London, 1970, p.341. Glaser was then professor at the Royal Botanic Garden in Paris and lectured on practical applications of chemistry, including the preparation of chemical drugs. The subject of chemistry embodied animal, vegetable and mineral matter, which, by fire was reduced to different substances; see Boas Hall, above.

2. ibid. ,342.

1.2 Continued

natural science.¹ Nevertheless, in the century which followed, the problem of what constituted a true classification and meaning of chemistry continued to pose considerable difficulties. Thomas Thomson's account of chemistry in 1830 included a chapter on those parts of chemistry which were already classified, and those which still awaited systematization.² 'In order to form a systematic nomenclature', wrote Thomson, 'it will speedily be requisite to new-model all the old names which denote acids and bases; because unless this is done, the names will become too numerous to be remembered.'³ Interestingly, Thomson was to include into the domains of chemistry, the animal and mineral kingdoms as well as physiology, disciplines so ardently denied by those like Libavius as belonging to the realms of chemical knowledge.

1. Pattison Muir, op.cit., ix.

2. T. Thomson, The History of Chemistry, London, 1830.

3. T. Thomson, op.cit. p.317, 318. According to Thomson, chemistry, unlike the other sciences, sprang originally from delusion and superstition, and was, at its commencement, exactly on a level with magic and astrology. 'It was long before it could shake off the trammels of alchymy, which hung about it like a night-mare, cramping and blunting all its energies, and exposing it to the scorn and contempt of the enlightened part of mankind', see his Introduction.

Indeed, Thomson's view of chemistry at the turn of the 19th century bears some remarkable points of similarity to those of the old alchemical schools. A conviction that, by means of controlling chemical processes 'mankind would be, in some measure, independent of climate situation; everything could be produced at pleasure in every part of the earth. Let the science advance for another century with the same rapidity that it has done during the last fifty years, and it will produce effects upon society of which the present race can form no adequate idea.'¹

Thomson's optimistic approach stands in marked contrast to that of many later works, both in his beliefs as to what chemistry stood for and what it could achieve. Lothar Meyer, in his introduction to the modern theories of chemistry, published only some thirty years after Thomson's work, took the premise, culled from Berthollet, that all the various chemical phenomena could be deduced from distinct and unalterable fundamental properties of matter.² Nevertheless, chemists were now compelled, Meyer thought, to examine chemical phenomena step by step and such

1. T. Thomson , op.cit., 318

2. L. Meyer, Modern Theories of Chemistry, 1862, trans. from the 4th edition by P. Bedson, W. Williams, London, 1888.

careful observations would show that these changes closely resembled the principles known in mechanics.¹ The ultimate aim of chemistry, as a branch of the natural sciences, was to seek the causal connection of phenomena in such a way that the resulting phenomena could in all possible cases be predicted from the given conditions. If chemical phenomena were not to be regarded as the result of the actions of chance, then clearly, Meyer wrote, they are 'subservient to the general principles of mechanics, to the laws of equilibrium and of motion.'² Thus, Meyer concluded, the ultimate understanding of chemical phenomena lay in the development of chemical statistics and mechanics.³ In the meantime, the newly discovered chemical compounds were to be the building material for modern chemistry, and Meyer affirmed, until these had been 'arranged and classified', no theory of chemistry was possible. Many of the problems of chemistry had been inherited because chemical terminology was in a state of confusion, the same word being frequently employed by different parties with exactly opposite meanings.⁴ 'The chemistry of the present day,' said Meyer, 'resembles a plant which, spreading its roots in the ground and

1. L. Meyer, op.cit. Introduction, xx.

2. ibid.

3. ibid.

4. ibid.xxvii.

collecting food, prepares for a later and quick growth of branches, leaves and fruit.¹ It appeared that, far from controlling chemical processes, as Thomson thought, full mastery of the subject was still an event of the future.

Some twenty years later, in the preface to the 4th Edition of the book, Meyer was pressed to introduce a new section dealing with chemical dynamics. The difficulty of the subject presented considerable problems to such an undertaking, far greater than Meyer had first imagined, aggravated by the fact that he considered the whole topic still not fully developed. In the interim between the first and fourth editions, it appeared to Meyer that the study of the influence of the mass on chemical reactions, first suggested by Berthollet, had not gained the attention of as many chemists as the subject warranted. The state of the science at that time, Meyer thought, was more akin to the conditions a hundred years ago than the majority of chemists imagined. Nevertheless, the importance of the subject of dynamics could not be ignored. Meyer firmly believed that a new doctrine of affinity was destined to result from a diligent study of mass action.² What was lacking, however, was sufficient attention being paid to the quantitative aspect of chemistry. Meyer thus advocated

1. L. Meyer, op.cit.

2. L. Meyer, op.cit., xvi.

1.2 Continued

that areas so far neglected, such as the effects of mass and temperature, be examined minutely, and that not only the compounds produced in chemical reactions, but also the reactions themselves be subjected to a quantitative scrutiny.¹

The study of chemical change was separated by Meyer into two groups, the dynamics of molecules, and the dynamics of atoms. This latter group included chemical changes which resulted from the formation of molecules into atoms and by several molecules uniting to form one single molecule.² It also included,

- a) One molecule decomposing into several molecules which may either be similar or dissimilar
- b) A molecule losing or gaining other atoms
- c) Substitution reactions
- d) Atoms in the molecule changing their mode of linkage.³

1. L. Meyer, op.cit., xvii.

2. ibid. ,358, 359.

3. ibid.

These are, in fact, similar to the major classification of reactions recognised today. However, as Meyer pointed out, these changes were not always straight forward, but often occurred simultaneously, rendering the resulting phenomena extremely complex.¹

Meyer's description of dynamic chemical change corresponds closely to the later concepts of 'reaction mechanism.' What was pre-requisite to the development of this branch of chemistry was the interpolation of the time element into the process of chemical change, an understanding of why specific chemical changes occurred at a specific rate and how they did so. In the different intervals of time taken by different chemical processes to go from reactants to products, lay the answer to the 'path' by which the reaction had occurred. As it was to emerge eventually, these chemical 'paths' were, almost invariably, not simple, one-step additions or substitutions, but consisted of a series of complex and consecutive chemical changes. The elucidation of the nature of these chemical changes was to be accomplished by the studies of chemists who turned their attention to studying the actual rate of chemical change. Among these were the two teams, Guldberg

1. Meyer, op.cit. ,358, 359.

1.2 Continued

and Waage, and Harcourt and Esson.

Meyer's concept of chemistry, spanning the years 1862-1888, is remarkable in several respects. The descriptions of chemical processes and chemical changes in general are indeed 'modern' in conception, compared to the language and method described in, say, the text of Thomson's, thirty years earlier. It is also notable that though Meyer's book discusses Guldberg and Waage's theory of mass action in some considerable detail,¹ the work of their contemporaries Harcourt and Esson is not mentioned. The Norwegians in fact investigated the complex phenomenon of chemical equilibrium, the attainment of which required considerable lengths of time; they also found that the lower the temperature, the greater the period of time required. But it is largely due to Harcourt's work that the idea of 'consecutive' chemical changes in a reaction finally became established, as we shall see. The reasons for Meyer's omission lay perhaps in the related social factors of the day, a question of communication, rather than any reflection on the relative importance of the contributions made by the two groups.

1. Meyer's account of Guldberg and Waage's work states that "they added to Berthollet's altogether too simple mass action theory, the influence of time, space, temperature and the strength of affinities on the chemical decomposition."

Meyer's chemical text rapidly went through four editions, and a fifth was demanded and achieved even as its English translation was proceeding.¹ Its influence on the German chemical scene was thus considerable, sufficient to warrant a complete translation, 'to make it as accessible to the English student of chemistry as it was to his contemporary in Germany'.² What is evident from Meyer's text is that the concept of reaction rates as a distinct field of chemical investigation took a considerable period of time to be accepted. Thus in the years immediately following the appearance of the papers by Guldberg and Waage, Harcourt and Esson, few references are made to their work.³ Meyer, in 1883, considered the new doctrine of the action of mass to be 'the direction of the science in the future', and, as such, still very incomplete.⁴

But the speed with which the development of this branch of investigation was to proceed in the last two decades of the 19th century can be partly gauged by a later chemical

1. Meyer, op.cit., Translators Preface.

2. ibid.

3. For a discussion on the influence of their respective work see later sections in this work.

4. Meyer, op.cit. xvii.

text. In Ernest von Meyer's account of the history of physical chemistry, the development of affinity theories already assumed a historical rather than the futuristic significance attributed to them by Lothar Meyer.¹ von Meyer's approach was perhaps encouraged by the appearance of works by Wilhelm Ostwald around that time, which frequently included references to chemical developments of historical significance.² Thus von Meyer traces theories of affinity from the time of Bergman onwards, emphasizing the revival of Berthollet's theory of affinity by Guldberg and Waage and the earlier idea of dynamic equilibrium by Alexander Williamson, in 1850.³

The work of Guldberg and Waage was of special significance, because, according to von Meyer, it had an extraordinarily stimulating effect on subsequent chemical investigation. Bringing the subject up to date, von Meyer also mentions the pioneering contributions of Horstmann, van't Hoff, Willard Gibbs, Chatelier, Duhem and Planck

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1. E. von Meyer, A History of Chemistry, from Earliest Times to the Present Day, trans. by G. McGowan, London 1906.
 2. See for example, W. Ostwald, Lehrbuch der Allgemeinen Chemie, 2nd. Ed., Leipzig, 1896-1902, Vol.2, Part 1, 67.
 3. ibid. ,553, 554.

1.2 Continued

in establishing the concept of chemical equilibrium.¹

'Hand in hand with this', wrote von Meyer, 'went other work upon the time required for chemical change, in other words, upon velocity of reaction. W. C. Wilhelmy had already clearly grasped the idea of this in his investigations but the conclusions he drew failed at the time to find acceptance.'² Von Meyer's surmise was highly accurate and in fact underlines one of the curious chapters in the development of chemical rate studies. Not only was Wilhelmy's investigation not accepted at the time, but even much later, when the speeds of reactions were being re-examined, the significance of his rate measurements remained unrecognised. The contributions of Wilhelmy, Williamson and van't Hoff to the establishment of time factors in chemistry will be discussed later in this work.

Two other works on the subject of chemical dynamics were to emerge with enormous influence on later investigators in the field of chemical reaction rates. These were the Études de Dynamique Chimique of J.H. van't Hoff, in 1884, and Chemical Statics and Dynamics by J.W. Mellor which appeared in 1904. Together, these two texts collated the ideas and results of large numbers of workers in the half

1. von Meyer, op.cit., 557

2. ibid.

1.2 Continued

century which had elapsed since the pioneering work of Wilhelmy in 1850, and finally established the concept of time in chemistry as a new, independent area of chemical research.

In a brief appraisal of what has constituted chemistry and chemical change at different periods of chemical developments, it is all too easy to see a continuous, orderly and progressive comprehension of the science. Yet it seems that chemistry was by no means a clear-cut, well-defined discipline even in the late 19th century. What linked the past with later views was that all considered chemistry to be the study of change of material things. Rodwell's concept of chemistry in the 19th century was 'distinctly and definitely the science which treats of the changes which matter undergoes; physics proper treats of action of various forces - heat, light, electricity, magnetism - upon matter, in all cases unaccompanied by any change of composition.....the idea of change is the fundamental chemical conception.'¹ It was a conception which was echoed by many chemists of that era. Pattison Muir, in his history of chemical theories and laws, wrote,

1. G.F. Rodwell, The Birth of Chemistry, London, 1874.

the essential object of the study (of chemistry) at all times may be expressed in the language of today as being to describe, to set in due order, and to connect the changes of composition and the changes of properties which occur simultaneously, in systems of homogeneous substances, and the conditions under which these changes proceed.¹

In the early years of the present century, Freund made a special attempt to define and categorize the nature of chemical change and the methods which could be employed for their elucidation.² Such attempts at classification were still wrought with difficulties, but difficulties which were of paramount importance to overcome for a systematic understanding of chemical philosophy to emerge. In an earlier historical study of chemical composition, Freund had already devoted a complete chapter to the classification of methods and laws in chemistry.³

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1. M.M. Pattison Muir, op.cit., viii.
 2. I. Freund, The Experimental Basis of Chemistry, Ed. by A. Hutchinson, M.B. Thomas, Cambridge, 1920.
 3. I. Freund, The Study of Chemical Composition, Cambridge, 1904.

As a branch of science, a subject which included 'all clearly defined facts of experience which are communicable and verifiable', - chemistry could be defined as:

the science dealing with the study of all the ^{different}/homogeneous kinds of matter met with in nature, and with the permanent changes these can undergo when transformed into other kinds of matter.¹

The emphasis placed by Freund on what constituted chemistry was that it should encompass a mode of permanent change. However, this definition, if taken literally, raises considerable problems when discussing, for example, reversible chemical change and the phenomenon of chemical equilibrium, two very important concepts in the development of chemical reaction rates. Nevertheless, the same view was held by others, like Jean Perrin, who considered irreversibility to be an integral part of the concept of chemical phenomena but that as soon as there was reversibility, the phenomenon was considered to be

1. I. Freund, The Study of Chemical Composition, p.2.

physical.¹ The idea of chemical equilibrium is a complex one, above all because it embodies the concept of a seemingly static state undergoing continuous dynamic change; a state which Ostwald defined, perhaps unwisely as being 'independent of time'.² It was generally considered then, that physics was concerned with the temporary, whilst chemistry dealt with the permanent changes which matter underwent.³ By inference, time was not a chemical factor.

Freund's methodic study stands out as a fairly contemporary attempt to give precision and meaning to what chemistry really was, and more important, was not. The fundamental distinction drawn between what constituted physics and chemistry was to have direct consequences on the evolution of ideas in chemical rates of reaction, a discipline which touched on both.

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1. J. Perrin, Traité de Chimie Physique, Paris, 1903, .10.
 2. W. Ostwald. "The Faraday Lecture", J. Chem. Soc., 1904, 85, 509.
 3. Freund, op.cit. 1920, 58.

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Part 2

2.1. The Origins of Chemical Rate Measurements

2.1.1. From Quality to Quantity. From Affinity to Chemical Equilibria

The quantification of physical phenomena has had a long history, a tradition which epitomises the concept of continuity in scientific thought.¹ In the period of the Renaissance especially, two dominant scientific doctrines were particularly evident: that all certain knowledge could be recognised by ~~its~~ quantitative characteristics and that perfect knowledge was always mathematical.²

In physical theory, it was the quantification of the macrocosmic world which was first to emerge, in the form of laws for planetary motion, long before the microscopic world of the atom could be understood. In this same period of development however, not all those engaged in scientific thought shared this conviction of mathematised knowledge as the ultimate goal. Ample examples of the conflict between mathematisation and its role in the search

1. See for example, E.A.Burtt, The Metaphysical Foundations of Modern Physical Science, London, 1932; G.Buchdahl, Metaphysics and the Philosophy of Science; The Classical Origins, Descartes to Kant, Oxford, 1969.

2. Descartes for instance saw science as comprising only knowledge that was certain and evident: Of the sciences known, only arithmetic and geometry were free from falsity and uncertainty. See A.Koyré, From the Closed World to the Infinite Universe, New York, 1958.

for true understanding of Nature are to be found, most frequently in the work of those concerned with the chemical sciences. Such a figure, for instance, we find in Johann van Helmont.

Although himself instrumental in developing two of the most vital advances in quantification, the thermometer and the pendulum, van Helmont appeared less than enthusiastic about the growing 'heathen' idea of reducing natural phenomena to that of mere numerical analysis. In his polemic against the Schoolmen, van Helmont was quite adamant that by reducing Nature to mathematics, man was departing further from the truth for which all were searching:

Indeed, whenever the Schoolmen conceive anything mathematically, they at once turn it into nature on the strength of a general validity of their rules. In this way, they confusely adapted to four fictitious elements, four qualities, complexions and humours; they have even applied these controversies to the stars and maintain that everything fits into their fiction.¹

1. W. Pagel, "J.B. van Helmont and 'De Tempore'", Isis, 1942, 33, 621. Van Helmont was particularly antagonistic about the Schoolmen's approach to the heavenly bodies, space and time which in his thoughts were associated with God. "No wonder", he wrote, "that by this method, they have brought their mathematical speculation about a continuum into line with the lineal points and finally with time." Pagel, op.cit.

Nevertheless, van Helmont's role in bringing quantification to chemistry was considerable. Partington, for instance, attributes to van Helmont the law of Conservation of Matter when the latter discovered that "the weights or masses of substances, recovered from compounds prepared from them are equal to the masses originally taken".¹

Quantification in chemistry has usually been associated with the search for affinity forces on the one hand and with Lavoisier's establishment of the Law of Mass Conservation on the other. But earlier, in his Sceptical Chymist of 1661, Boyle was strongly advocating not only 'how much' and 'how many', but also 'why'. He wrote,

how will the knowledge of Tria Prima discover
to us the reason why the loadestone drawes a
Needle, and disposes it to respect the Poles and
yet seldom precisely points at them? How will
this hypothesis teach us how a chick formed in
the Egge, or how the seminal principles of mint,
pompions and other vegetables, can fashion water

1 J.R. Partington, "The Concepts of Substance and Chemical Elements", Chymia, 1948, 1, 114-115.

into various plants, each of them endow'd with it's peculiar and determinate shape?¹

As history has shown, Boyle attempted to answer his speculative reasonings by the procedure of logical experimental investigation.² As a natural philosopher, advocating the seriousness of chemistry, Boyle was convinced of the importance to chemistry of quantification and of mathematical methods in the understanding of natural phenomena.

But here I might not forget to take notice that I can scarce think men will be able to know all the propertys and uses even of familiar Bodys and other things, 'till they have mathematically considere'd them there being several attributes belonging to even such things which a naturalist tho' curious will probably never find out unlesse he be both

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1. R. Boyle, The Sceptical Chymist, 1661, (2nd edition) Reprinted as Everymans Edition, London, 1911; New York 1937.
 2. The full title of Boyle's book (2nd Edition) is of significance in showing his approach to chemical practices: "The Skeptical Chymist: Or Chymico-Physical Doubts and Paradoxes, touching the Experiments Whereby Vulgar Spagirists are wont to Endeavour to evince their Salt, Sulphur, and Mercury; To be the True Principles of Things. To which in this Edition are subjoin'd divers Experiments and Notes about the Producibleness of Chymical Principles."

acquainted with mathematical Disciplines, and have the curiosity to apply them to Phisicall subjects.¹

Boyle recalled that Galileo set a pattern for the advancement of physics when he discovered a natural law governing temporal flux. Although countless persons had had occasion to observe the motion of swinging bodies, until Galileo (whom Boyle believed to be the discoverer) took notice of the vibrations with mathematical eyes, the exact properties of pendulum motion remained unknown. And the good derived from this mathematical observation had been enormous.

As a chemist, Boyle's attitude towards the importance of quantification in chemistry was probably influenced, to no small degree, by the mathematical figures, like Wren, with whom he associated. It has been observed that he was, for instance, well acquainted with the dynamic principles of Descartes' Principia Philosophiae.² What is perhaps all too easily overlooked is the fact that Boyle's firm belief in the necessity of quantified chemistry coincided with an era when the meaning and even existence of the

1. R. Boyle "Of the Usefulness of Mathematics for Natural Philosophy", quoted in M. Boas, Robert Boyle and 17th Century Chemistry, Cambridge, 1958.

2. ibid.

subject was far from being established.¹ Boyle was to write on more than one occasion in defence of its respectability, with the wish and determination to establish that chemistry was the key to natural philosophy. The search for a definition and a specific meaning to the domains of chemistry was, as we have seen, to occupy the thoughts of many chemists throughout the centuries. The dilemma as to the true identity of chemistry was intimately, though subtly, connected with the problem of how to make chemistry an 'exact' science, and a quantified discipline.

The history of early quantification in chemistry has most frequently been associated with the evolution of the study of Matter, and the time when chemistry became recognized as an 'exact' science is usually referred to as the age of Lavoisier. Quantification in chemistry thus became, in one science historian's view, a concern to (a) characterize common substances (b) delimit classes of substances (c) determine the relationship of elementary substances making up compounds and (d) to explore relations among the elements themselves.² Indeed, this was very much how, in the main, chemistry was to evolve from the time of van Helmont and Boyle to the middle of the 19th century. Unlike physics, which was primarily concerned with

1. Thus Boyle's contemporaries lamented that their honourable friend 'one who could contribute to respectable natural philosophy should expend his energies on what was at best only an adjunct to the other sciences, and at worst alchemy' see M. Boas, Robert Boyle, 48.

2. H. Guerlac, "Quantification in Chemistry", Isis, 1961, 52, 197.

mathematical generalisations about phenomena and their causes, chemistry was to retain its dependence on quality.¹

As we shall have cause to reiterate frequently in this present work, chemists were, for the most part, overwhelmingly concerned with the nature of matter itself, rather than with questions of its origins or its end.

The science of the 17th and 18th centuries has frequently been described as being predominantly occupied with a mechanical philosophy.² It was a philosophy which, though physical in origin, was also to give direction and impetus to chemistry. Chemists saw in its realization the hope at last of achieving a quantified chemical force, the age-old question of affinity finally resolved. In keeping with the times, the physical model for chemical mathematization was the Newtonian philosophy - based on universal gravitation. Chemists became increasingly convinced that the specificity of chemical reactions was capable of explanations based on the familiar concepts of attraction and repulsion between substances. Fourcroy was stating with confidence in 1787, that

all chemistry reduces to an exact knowledge of

1. So much so that Guerlac maintains chemistry has retained this qualitative goal even after the advent of physical chemistry, ibid. , 196.

2. See for example E.J. Dijksterhuis, The Mechanization of the World Picture, Oxford, 1969.

the elective attractions between natural bodies. When the strength of this force between all natural substances has been determined, chemistry will be as complete as it possibly can be.¹

Such sentiments were to dominate the thoughts of many chemists for certainly the greater part of the 18th century; an age when much of the theoretical arguments and practical efforts were based on the firm belief that 'if chemistry was to be made a predictive, quantitative science, then it would be through the experimental measurement of short-range attractive forces'.²

It cannot be thought, however, that all chemists were united in this Newtonian belief - that the specificity of chemical reactions could be explained entirely in terms of degrees of differing attractive forces between different reacting substances. The argument as to whether it was correct, in the first place, to transport a theory of physics and apply it literally to chemical systems was still unabated. Men like Boerhaave, William Lewis and Stahl opposed the idea, whilst Buffon supported it.³ Buffon appears to have seen

1. Quoted in: A. Thackray, Atoms and Powers, Oxford, 1970.

2. ibid., p.202. Thackray's expression 'predictive, quantitative science' is an interesting choice. The role of prediction in chemistry will be discussed in the later section on chemistry and philosophy.

3. See J.R. Partington, A History of Chemistry, London, 1964, Vol. 4, p.569; 1961, Vol. 2, p. 665.

chemical progress as a natural ancillary to physics, Newtonian physics, for he observed,

the obscurity of chemistry results in great measure from its principles being insufficiently generalized, and not united to the higher physics.¹

Universal attraction was, to Buffon, the ultimate goal in answering the problems of chemical specificity. And, although these answers were far from complete, he clearly believed that the laws of chemical affinity were the beginnings of a great chemical understanding, the 'new key' which would enable chemists to explore the deepest secrets of nature. Lewis, on the other hand, was convinced that chemistry was a distinct science, for which Newtonian speculations had little relevance or value.²

natural or mechanical philosophy seems to consider bodies chiefly as being entire aggregations or masses---subject to mechanical laws, and reducible to mathematical calculation. Chemistry considers bodies as being composed of such a particular species of matter and with properties which are not subject to any known mechanism, and seem to be governed by laws of another kind. The

1. Quoted by Thackray, op. cit. ,216.

2. William Lewis, 1708-1781, physician at Kingston-on-Thames, lectured to the Prince of Wales at Kew.

other branches of knowledge are concerned with attraction in mechanical philosophy and affinity in chemistry.¹

Lewis firmly believed that the effects of the last mentioned, i.e. affinity in chemistry, could be deduced from simple facts, not reducible to any known mechanism nor were they capable of investigation by any principles, other than by direct observation.² This view of chemical phenomena as being intrinsically empirical in nature was by no means peculiar to Lewis. In fact it might be said to have typified a school of thought supported by all those who were not totally convinced by the Newtonian vision of quantified chemistry.

The fact that this Newtonian dream did not ultimately survive was due, certainly in part, to the over-simplification of the assumptions associated with the original concepts. Even with all the evident enthusiasm supporting it, the very foundations on which the laws were laid were insufficiently secure to account for the problems being encountered in reality; as we can now see simple laws of affinity failed, perhaps because they were too simple, and did not resolve the problems presented by, even at times, obviously important factors within the complex domains of chemical reactions.

1. J.R.Partington, op. cit. Vol. 2, 763.

2. ibid.

Factors such as temperature and concentration of reactants in chemical processes could not very easily be ignored.¹

Such ideas, however, were to lead nowhere, perhaps one of the dangers of taking the analogy between chemical and physical systems too literally. For if gravitation was truly universal, there was no reason why factors such as temperature ought to play a major role, which it certainly did not in Newton's physics. Such omissions were too obvious to last for long. Whatever the extent of its influence on later chemical progress, Newtonian chemistry in the form of universal gravitation had but a relatively short life-span. As Thackray put it, 'the slowly dawning realisation that these assumptions were too simple was to be one of the reasons for the widespread disenchantment with the Newtonian vision apparent toward the close of the century.'²

Nevertheless, the search for the elusive forces of affinity remained the chemical goal, to be pursued well into the following century, when chemists like Guldberg and Waage sought to establish the laws of chemical affinity. The difficulties presented by quantification of the affinity forces were manifold. Apart from the innate complexity of chemical systems, the application of higher mathematics was, and remained, outside the average abilities of the majority

1. Thackray believes that chemists were also considering the influence of concentration on the rate of chemical reaction at the time. There is little evidence for this, although Wenzel did consider affinity forces by observing rates of dissolution of metals in acid, see later.

2. A. Thackray, op. cit., 203.

of even trained chemists.¹ It was perhaps to contribute, not inconsiderably, to the picture of a delayed revolution in making chemistry an exact quantified science. In the 18th century, even the most ardent advocate of the Newtonian vision of a quantified chemistry, like the French chemist, P.J. Macquer, had to admit the superficiality of his own treatment and the difficulties which lay ahead for chemists before the dream could be realized. It first required 'the zeal of persons skilled in mathematics and chemistry'.²

This symbiosis was to give rise to the establishment of a new discipline, that of physical chemistry, in the latter half of the 19th century.³ The leading figures who formally made mathematics an indispensable part of the search for understanding chemical phenomena were Ostwald, van't Hoff and Arrhenius. In 1914, Arrhenius was to extend this synthesis to embrace another emerging discipline, biological

1. This lack of mathematical training for chemists was notable in the 19th century establishment of chemical rates of reaction. Both the pioneering teams in this field, Guldberg/Waage and Harcourt/Esson comprised a chemist and a mathematician.

2. A. Thackray, op.cit., p.210. D.W. Theobald believes that Thackray's book shows that 'progress in chemistry is not linked with an uncritical pre-occupation with quantitative reductive analysis', Chem. Soc. Reviews, 1976, 5, 208.

3. For an interesting account of the emergence of physical chemistry see for example R.G.A. Dolby, 'The Emergence of a speciality, a case study: physical chemistry', Actes du XII^e Congrès Internationale d'Histoire des Sciences, Paris, 1968, 29-32.

chemistry. His introduction summarized well the attitudes of a new generation of chemists working on a quantified science:

As long as only qualitative methods are used in a branch of science, this cannot rise to a higher stage than the descriptive one. This was the position of chemistry in the alchemistic and phlogistic time before Dalton had introduced and Berzelius carried through the atomic theory, according to which the quantitative composition of chemical compounds might be determined, and before Lavoisier had proved the quantitative constancy of mass.¹

In even stronger terms, Arrhenius maintained that no real chemical science in the modern sense of the word existed before quantitative measurements were introduced.² In short, chemistry which had consisted of a large number of descriptions of known substances and their use, their occurrence and their preparation in accordance with well established recipes constituted merely the hermetic (or occult) art.³

But even before the emergence of physical chemistry as a distinct chemical discipline, its foundations were being laid by the application of mathematical theory to chemical phenomena.⁴ The pioneers were either physicists

1. S. Arrhenius, Quantitative Laws in Biological Chemistry, London, 1915, 1.

2. ibid.

3. S. Arrhenius, op.cit., 2.

4. The identity of physical chemistry as a speciality is dated as 1887, when Zeitschrift für Physikalische Chemie was first founded, see Dolby, op.cit. 30.

like Wilhelmy or teams of chemists and mathematicians like Guldberg and Waage or Harcourt and Esson, whose contributions to quantified chemistry will be discussed in subsequent sections. In the meantime, unlike the Newtonian vision of universal gravitation, which gradually but surely faded into oblivion, the other Newtonian concept, that of balanced forces, was to lead to a radically new chemical ideology.

There is little doubt that the concept of chemical equilibria and the associated process of reversibility in reactions, form one of the most fundamental ideas to have evolved in the development of chemistry. The realisation that if, in some reaction, $A+B$ proceeded to $C+D$, the reverse was also possible, was followed by the discovery that these two reactions could be occurring simultaneously. The phenomenon of reversible reaction was, very probably, observed empirically by early chemists.¹ Explanations for their occurrence however were not so simple, although Regnault in 1836, related them to the effect of mass action.² The idea of contending

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1. As early as the mid and late 18th century, Baume and Cornette had studied the reversible actions of acids and salts see J.R. Partington, A History of Chemistry, London, 1964, Vol.4; 576; Vol.3, 92,100. Gay-Lussac, in 1816, discovered that the action of steam on metals, such as iron, was reversible.
 2. V. Regnault, 'Recherches relatives à l'Action de la Vapeur d'Eau à une haute température sur les Metaux', Ann. chim. et phys., 1836, (2nd ser) 62, 337-374.

forces as being responsible for chemical action was, on the other hand, not so far removed from the familiar idea of Newtonian attraction. Observing a metal when heated in concentrated sulphuric acid, Lavoisier noted that the 'oxygen' of the acid,

must be considered as obedient to two unequal forces; on the one part it is attracted by the metal which tends to calcination, that is to say, to become oxide, and on the other hand it is retained by the sulphur, and it is divided into two parts until an equilibrium is reached.¹

Two years previously, in his Méthode de Nomenclature Chimique of 1787, Lavoisier had considered the question of combining proportions in chemical compounds, noting that the acidifying and acidified principle can exist in different proportions, which constitute the points of equilibrium and of saturation.² The general principle of opposing forces could be applied, with equal logic, to both physical and chemical phenomena as Lavoisier observed:

Thus we have to consider the constituent molecules of the substructures as obeying two forces, the calorique which tends continuously to disperse them, and the

1. Quoted in Partington, op. cit., Vol. 3, 644.

2. Partington, op. cit., Vol. 3, 644.

attraction which counterbalances this force.

When the attraction is victorious, the substance remains solid. When these two forces are in a state of equilibrium, then the substance becomes liquid.¹

It is Berthollet, however, who is credited with the first clear statement of the idea of chemical equilibrium. His ideas on affinity and the influence of quantity in chemical reactions are contained mainly in his two books, Récherches sur les Lois de l'Affinité, first published in 1801, and Essai de Statique Chimique of 1803. These works together formed the basis of the later ideas by Guldberg and Waage in establishing the law of 'mass action'.

The origin of Berthollet's ideas on mass action is not very clear.² He clearly realised that, very frequently, chemical reactions did not proceed to completion, and that the affinity theories, principally those of Bergman, were insufficient to explain many of the contradictions of experimental data. As early as 1776, he wrote of his dissatisfaction with the existing laws of chemical combination. As he put it,

It is not that I believe that there are no constant laws which bodies obey in their combination, in their union, in their

1. A. Lavoisier, Mémoires, 1805, Vol. 2, p.4-7.

2. Mellor's suggestion that Berthollet was struck by his observations of the large deposits of sodium carbonate found on the Natron lakes in Egypt is not well founded, as pointed out by Lindauer, J. Chem-Ed., 1962, 39, 385.

decomposition; but we are very far from being sufficiently advanced to foresee all the circumstances which cause these laws to vary, and to be able to construct a general system of affinities.¹

Just over twenty years later, Berthollet published his Récherches, in which he outlined ideas on the action of mass in chemical reactions. He proposed that, in general, 'elective affinity' did not act as the sole determinate force holding bodies together. In any chemical combination, the activity of a substance is a product of both its affinity and the quantity of it in contact with the other reactants. Thus if two substances are both reacting to combine with a third substance for which they have unequal affinity, the weaker affinity could be compensated if it were present in sufficiently large quantity.² Berthollet defined his meaning of mass in the first article of the Récherches:

if I can prove that a weaker degree of affinity can be compensated by an increase of quantity, it will follow that the action of any body is proportionate to the quantity of it which is necessary to produce a certain degree of saturation. This quantity, which is the measure of the capacity of saturation of different bodies, I shall call mass.³

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1. Quoted in J.R.Partington, A History of Chemistry, London, 1902, Vol.3, 645.
 2. C.L.Berthollet, Récherches sur les Lois de l'affinite, Paris, 1801, translated by M.Farrell, London, 1804, Art.1(5).
 3. ibid.

Berthollet's recognition that chemical reactions often do not tend to completion was accompanied by the discovery that reactions could be reversed if the conditions were reversed. Thus, lime acting on the carbonate of potash could not entirely decompose the combination, even by the addition of excess of lime. His experiments showed that the reverse effect could be brought about by changing the conditions, that is, the decomposition of the carbonate of lime by the action of potash, when present in sufficient quantities.¹

He wrote:

the only difference between the two operations consists in the different quantities of the two substances which it is necessary to employ, in order to produce the opposite effects.²

Berthollet expressed the idea of this reversible chemical action in terms of two antagonistic forces, acting in opposition, until the equilibrium of the contending forces ends the operation and limits the effect.³

Thus Berthollet had introduced two critical ideas, which were to find expression in chemical theory only much later. Firstly, contrary to popular 18th century chemical belief, he proposed that chemical action was conditioned not only by the affinity but also by the relative masses of the reacting bodies. Secondly, a chemical change could be reversed by altering the relative quantities (masses) of the reacting bodies, that is,

1. C.L. Berthollet, op. cit., Art. III, 1.

2. ibid.

3. Recherches, op. cit., Art. 2, 9, 10.

chemical reactions did not always proceed in one direction.

Berthollet's original contributions were, however, not fully appreciated by his contemporaries. Many later authors have commented that the reasons for this could be traced to Berthollet's controversial *mêlée* with Proust over the law of chemical combinations, in which Berthollet was defeated,¹ and with it, any serious consideration of his other achievements. But it must be added that the concept of chemical equilibria was a complex one and was not, perhaps, fully understood, even at the beginning of the present century. Pattison Muir, writing in 1907, commented,

He who would describe in detail the historical development of the study of chemical equilibrium must be a chemist, a physicist and a mathematician; he must be a man of great learning, vast audacity, and much literary ability. I know that I am quite unable to attempt the task.²

1. See L. Meyer, Modern Theories of Chemistry, 1862, trans. by P. Bedson, W. Williams from the 4th German Edition, London, 1888, xxiii; J.W. Mellor, op. cit., 178.

2. M.M. Pattison Muir, A History of Chemical Theories and Laws, Cambridge, 1907, 431. F.L. Holmes has written an interesting account of Berthollet's role in establishing the law of mass action, see From Elective Affinities to Chemical Equilibria: Berthollet's Law of Mass Action, Chymia, 1963, 8, 104-145.

Certainly the importance of Berthollet's ideas cannot be denied. In part, the failure of these ideas to make any immediate impact was due to the fact that he was unable to express the influence of mass and its effects in a quantified, mathematical manner, a task which had to await the work of Guldberg and Waage half a century later. Intuitively, however, his reasoning was to lead to a new bridge between chemistry and physics which was notably missing in the Newtonian vision of chemical quantification. As Lothar Meyer put it, 'If chemical phenomena are not to be regarded as resulting from the actions of chance, then it must be acknowledged that they are subservient to the general principles of mechanics, to the laws of equilibrium and motion.'¹ Writing in 1862, Meyer expressed a view which showed how the emphasis had shifted from Fourcroy's sentiment, a century earlier.² No longer expressed as elective affinities, the 'highest and final aim of all chemical investigation must be the development of chemical statics and mechanics; the doctrine of equilibrium of chemical forces, and of the motion of matter under their influence.'³

The concept of dynamic equilibrium was due largely to Alexander Williamson, whose work on the synthesis of ethers

1. L. Meyer, op. cit. p.xx

2. See this work, 67/8.

3. L. Meyer, op. cit. xx

will be discussed later. His frequently quoted paper of 1850 proposed that atoms and radicals of any molecule are in constant motion and undergo exchange with neighbouring molecules.¹ History shows, however, that the final establishment of the law of mass action and the first mathematical statement of chemical equilibria was to evolve directly from Berthollet's earlier ideas. This may have been due, in part, to the influence of Bunsen, who in 1853, drew attention to the French chemist's work by investigating the influence of mass in the distribution of oxygen in the reaction with two combustible gases.² The Norwegian chemist Peter Waage was to return to the University of Oslo from the laboratories of Bunsen in Heidelberg, around 1862, to commence work on chemical affinity and equilibria.³

1. A. Williamson, Phil. Mag., 1850, 37, 354. J. Malaguti also investigated the mutual decomposition of salts using the principle of dynamic equilibria, Ann. Chim. Phys., 1853, 3, 37, 198. Meyer believed his methods to be erroneous, see L. Meyer, op. cit., p.464.

2. R. Bunsen, Liebig's Annalen, 1853, LXXXV, 137.

3. The real origins of their ideas relating to chemical equilibria are, however, not clear. J.H. van't Hoff, himself a pioneer in chemical dynamics, associated its first study with Pfaundler. 'The study of chemical equilibrium yields results which form a very important addition to our knowledge of chemical change. This will be obvious if, with Pfaundler, we regard equilibrium as the result of two changes taking place in opposite directions with equal velocities' : Studies in Chemical Dynamics, London, 1896, 143.

In historical perspective, the role of quantification in chemistry does not appear yet to have been examined closely, except in connection with the properties of mass, mentioned earlier. For physics, the evolution of quantification has been traced to various periods in the development of its history.¹ Philosophically, however, the process involved in moving from an understanding of quality to that of quantity was common to both chemistry and physics. The measurement of the phenomenon of change appears to have emerged only gradually, indicating a distinct passage from the 'primitive' to the 'sophisticated'. As Meyerson put it,

every time that we pass from a quality to a quantity, we move away from the sensation and substitute for it more and more, a hypothetical concept. When instead of Aristotle's hot and cold, we introduce, first, heat and then caloric fluid, we have already created a highly abstract concept - it creates in us at least

1. See: Quantification, A History of the Meaning of Measurement in the Natural and Social Sciences, ed. H. Woolf, 1961, New York. More recently, the transformation of experimental physics from a qualitative expository science into a rigorous mathematized discipline in the first decade of the 19th century has been discussed by E. Frankel in J.B. Biot and the Mathematization of Experimental Physics in Napoleonic France, Historical Studies in the Physical Sciences, ed. by R. McCormach, L. Pyenson, Johns Hopkins University Press, 1977, Vol. 8, 33-72.

three highly characteristic sensations - cold, hot, burn.¹

The development of the familiar quantity of hot and cold to include heat has been taken as a progression in human awareness. The acceptance of two sensations as fundamental as hot/cold is much easier to comprehend than those of heat and heat flow; and the degree of sophistication is intensified in distinguishing heat flow as movement, a form of energy. In the development of science generally, 'it is by substituting for the sensation what is supposed to be its cause, that progress has been brought about'.²

In an analogous manner, the development of the concept of mass and quantity in chemical reaction, as visualized by Berthollet, and quantified later by Guldberg and Waage, were distinct phases in the evolution of chemistry. However, these ideas retained, to some degree, the features of an initial, intrinsic 'sensation' or 'substance' of the quantity. The development of modern chemical theory also involved the search for an understanding of how chemical reactions come about, and of why they proceeded in a specific manner, as observed experimentally; that is, for causality. Causality in chemistry may indeed be different from that in physics, deriving not from a single factor, but, as Vernon Harcourt was to write, from the whole course of a chemical reaction. Chemical causality is therefore justifiably related to the development of the course of chemical change as embodied in reaction velocities and mechanisms, and the concept of chemical reaction as a dynamic phenomenon.

1. E. Meyerson, Identity and Reality, trans. by K. Loewenberg, London, 1969. (1st. ed. 1930)

2. Meyerson, op.cit.

Before turning to a discussion of these developments, it is necessary to see how the methods, by which the rates of chemical reactions became quantified, were first conceived.

2.1.2 Chemical Affinity and Reaction Rates

Although the establishment of rates of reaction in chemistry was to emerge only rather indirectly from Berthollet's studies on affinity and mass action, the eighteenth century did see a number of links between affinity and speed of reaction. The speed with which chemical reactions were accomplished in the determination of chemical affinities had attracted the attention of Carl Wenzel as early as 1777, only two years after Bergaman's famous treatise on elective affinities.¹ In his work, Lehre von der Verwandtschaft der Körper, Theory of the Affinities of Bodies, published that year, Wenzel included a collection of his analysis of salts which was of sufficient note to be included by Guyton de Morveau in his work on affinity alongside those of Bergman's and Kirwan.² Combining his ideas on forces with Buffon's speculations about the shape of corpuscles, Wenzel concluded that bodies could be arranged in the order of their affinities for a common solvent, which would be in the inverse order of the time of dissolution. In one experiment he describes the rate at which dilute acids attacked metal cylinders; if, he wrote, an acid dissolves one

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1. Carl Friedrich Wenzel (1740-1793). Studied medicine and surgery in Amsterdam, and until 1766 was a ship's surgeon in the service of the Dutch Navy. He later studied chemistry and metallurgy in Leipzig. See R. Wunderlich, J. Chem. Ed. 1950, 27, 56-9.
 2. J.R. Partington, A History of Chemistry, London, 1962 Vol.3, 671.

drachm of copper or zinc in an hour, an acid of half the strength requires two hours, when the surfaces and heat remain equal.¹ Wenzel's results were not sufficiently rigorous to have made much impact at the time. By deducing that the "strength" of a chemical reaction is proportional to the concentration of the reacting substances, he had implied a form of the law of mass action. His ideas however, failed to influence the subsequent development of rates of reaction. Whether this was partly due to his belief in alchemy, published in a work some three years earlier, is doubtful but Partington at least believes that the publication contained absurd statements which injured his reputation.² Ostwald, on the other hand, believed that the reason for the long interlude between Wenzel's work and that of Wilhelmy in 1850 was because chemists were simply far too preoccupied with other problems.³

Earlier still, Wilhelm Homberg had attempted to take into consideration the effects of time factors on chemical reactions.⁴ Homberg carried out considerable numbers of quantitative experiments on the neutralisation of acids and bases including the first determination of equivalent weights.⁵ In 1700, he published his Observations sur la Quantité d'acides absorbez par les Alcalis Terreux. From his experiments,

1. J.R. Partington; op. cit., 1962, Vol. 3, 673.

2. ibid., 671.

3. W. Ostwald, L'Evolution d'une science - La Chimie, Paris, 1909, 259.

4. Wilhelm Homberg (1652-1715) see Partington, op. cit., Vol 3, 44, 46/ the most eclectic of chemists, studied science and medicine at Padua and Bologna. In 1704, Homberg became physician to the Duke of Orleans. See M. Boas Hall, Dic. of Scientific Biography, Vol. 6, 477 - 478.

5. J.R. Partington, op. cit., Vol. 3, 44.

Homberg concluded that,

The different quantities of each alkali necessary to absorb the same quantity of an acid...are the measure of the passive force of each alkali, and to render this measure more precise it is necessary to add further (the amount of) time required by each alkali to absorb the acids.¹

The "passive force" to which Homberg alludes is the quantity of acid required to neutralise the alkali; thus the weights of the same alkali which neutralise identical weights of different acids measure the 'active force' of each acid, whilst the weights of the same acid which neutralise identical weights of different alkalis measure the "passive force" of each alkali.

Like Wenzel, Homberg, who once worked in the laboratories of Robert Boyle, as well as in the splendid laboratories of the Duke of Orleans, believed in the possibility of the transmutation of metals. Time, Homberg thought, was all that was needed to convert silver to gold by repeating cupellations, when the particles of silver surround themselves with the matter of light and became gold. True to the spirit of the day, Homberg's :

chemistry was the art of reducing compound bodies into their principles by means of fire, and composing new bodies in the fire by the mixture of different matters. His 'alkalis'

1. J.R. Partington, op. cit., Vol. 3, 46.

were composed of crabs' eyes, coral, mother
of pearl, oyster shells, calcined hartshorn
and other alchemical sources.¹

The quantification of time in chemical processes was to be
truly conceptualised only much later.

1. J.R. Partington, op. cit., Vol. 3, 46.

2.1.3. The Development of Physical Rate Measurements

The work of Homberg and Wenzel on the speed of chemical reactions was rooted in the familiar grounds of chemical empiricism of that era. In the same interim, developments in physics had followed a somewhat different path. Röemer's deduction in 1676, that light took a finite time to reach earth, at a speed of 200,000 miles a second, was confirmed and extended by the optical interference studies of Fizeau in 1849.¹ Light was a feature of the study of astronomy, its understanding and measurement a necessary precursor to the study of Heavenly Bodies. Perhaps this explains the early date at which the velocity measurement was achieved. Rate studies on closer, terrestrial phenomena such as heat, electricity and magnetism were yet to follow.

Detailed, but largely still empirical studies on heat had been accumulated, notably by Joseph Black around 1762, and by Dulong, Petit and Fourier during the early part of the 19th century. Earlier still, the theory relating the rate at which hot bodies cooled had been given by Newton.² Hot bodies, when exposed to constant cooling, such as a current of air, lose a quantity of heat at any instant proportional

1. Terrestrial methods of measuring the velocity of light had been suggested in the intervening years, including that by Arago in 1838.

2. Phil. Trans., 1701, cclxx, 824.

to the excess of its temperature over that of the ambient air. Newton considered that consequent losses of heat in equal and successive intervals of time ought to follow a decreasing geometrical progression. On this theory, however, hot bodies would take an infinite time to cool down to the temperature of the surroundings, as several workers of the time noted. In fact, Newton's law could only be applied where the temperatures were not much above 200 degrees but deviated rapidly at higher temperatures.

In a series of time experiments published in 1739, Martine endeavoured to show that the true loss of heat with time was dependent on two different rates, one a geometric progression as envisaged by Newton, the other an arithmetical progression. The sum of the two series came very close to the heat losses as shown by experiments.¹ A mathematical expression for the rate of cooling in a differential form was derived by J.H. Lambert in 1778, in the form

$$du / dt = -au,$$

where u is the temperature above that of the surroundings, t the time, and a a factor which accounted for the nature of the body and its environment.² This differential form of the changes in a phenomenon with time was to form the basis of Wilhelmy's rate studies on sugars some seventy years later.

1. From: 'Essay on the Heating and Cooling of Bodies', reference given by T. Thomson in A System of Chemistry, (6th Edition), Edinburgh, 1820, Part 1, 109

2. J.H. Lambert, 'Pyrometrie', Berlin, 1778.

The time related experimental techniques contrived by the pioneering investigators of heat phenomena were outstandingly simple but their results were to be extremely far-reaching. Joseph Black, in his famous lectures of 1762, investigated the melting of ice by comparing time intervals in an attempt to discover the amount of heat which was concealed in the water.¹ When ice at 22 degrees Fahrenheit was brought into a warm room, after only a short interval, it was heated to 32 degrees, the freezing point, when it began to melt. But the process, Black noted, took place very slowly and several hours passed before the whole quantity of ice melted. Yet during the whole of this time, its temperature remained at 32 degrees, despite the fact that 'caloric' must have constantly entered the system. This 'caloric', Black found, was not indicated by the thermometer, so what had become of it?

Black suspended two thin, equal glass globes, both filled with water, in a large hall at an almost constant temperature of 47 degrees. The water in one globe was frozen to solid ice, and the other cooled to 33 degrees. In half an hour, the thermometer placed in the water rose from 33 degrees to 40 degrees but the time taken for the ice to reach the same temperature was $10\frac{1}{2}$ hours. Black reasoned that ^{more} 21 times the amount of heat was required for melting the ice and to raise

1. Joseph Black, 1728-1799, see N.F. Magie, A Source Book in Physics, New York, 1935, 134.

the temperature from the original 32 degrees to 40 degrees than that required by water, and calculated the units of heat absorbed by the ice in order to melt it.¹ By comparing time intervals in similar experiments, Black also measured the latent heat of steam.²

The conducting powers of gases were investigated by Dalton and in greater detail by Dulong and Petit. Dalton established that the difference in the time of cooling for a hot body plunged into different gases depended solely upon the conducting powers of the respective gases.³ Some years later, in a series of papers for which they were awarded the prize of the Paris Academy of Sciences, Dulong and Petit derived new relations between time and temperature which provided an exponential form of rates of change,

$$\frac{dT}{dt} = \log m T (a + 2ft). \quad 4$$

The early years of the 19th century saw a prodigious output on theories of heat which, in a relatively short time,

1. J. Black, Lectures of the Elements of Chemistry, Vol. 1, Edinburgh, 1803.

2. Heat experiments were not all carried out with such arithmetical precision. That air was a very bad conductor of heat was strikingly demonstrated by a human 'time' experiment recorded in Phil.Trans., of 1775 (3, p.484). Dr Fordyce, in company with Sir Joseph Banks, Sir Charles Blagden and other gentlemen volunteered into a room heated to the temperature of 260 degrees and found they could remain in it for some time without inconvenience.

3. J. Dalton, A New System of Chemical Philosophy, London, 1808, ^{vol.1} 117.

4. Ann.Chim.Phys., 1817, 7, 223; 1, 64.

put this 'imponderable body' in a unique position. During the first decade of that century, the rates of heat losses by radiation, particularly black body radiation, were established, notably by Leslie and Rumford. The work of Joseph Fourier in 1823 and that of Robert Mayer some twenty years later formed a continuity which was to lead to the evolution of thermodynamics and a new scientific discipline.¹ During this period of development, the relationship which emerged between temperature and time was to provide the mathematical basis for relating time to chemical change. Ludwig Wilhelmy's work of 1850 followed in this tradition.

2.1.4. The Work of Ludwig Wilhelmy (1812-1864)

The beginning of rate studies in chemical reactions is usually attributed to the studies of Ludwig Ferdinand Wilhelmy, published in 1850. At the time of this work, Wilhelmy had only recently taken up his post as a privat-dozent at Heidelberg, where he was to remain for only five years, before retiring.² His training, in both chemistry and physics, had also taken him to Berlin and Giesen.

Until this time, Wilhelmy's work had been primarily

1. For an analysis of Fourier's work on heat, see R.M. Friedman, 'The Creation of a New Science: Joseph Fourier's Analytical Theory of Heat', Hist. Studies in the Phys. Sci., Ed. by R. McCormack, L. Pyenson, Johns Hopkins University Press, 1977, Vol. 8, 73.

2. S. J. Kopperl in C. C. Gillèspeie (Ed.), Dictionary of Scientific Biography, Vol. 14, 359-360.

in the field of heat theory, particularly thermal conductivity, radiant heat and surface tension.¹ The work of Regnault, with whom he had studied in Paris, was to influence Wilhelmy's work at Heidelberg, where his inaugural dissertation dealt with the topic of heat and cohesion.² Thus both mathematics and the physical theory of heat were familiar to Wilhelmy and occupied much of his time before the publication of his work on chemical rates.³ He chose for chemical investigation the hydrolysis of sucrose in acid solution.

The inversion of cane sugar in solution had been studied from the beginning of the 19th century, combined with the study of optical polarization.⁴ The polarization of light had been known since Hüygens announced it in 1690 and had been sustained in numerous studies throughout the following centuries, since it had provided a fulcrum on which the controversy of wave versus corpuscular theories of light rested.⁵

1. See J.R. Partington, op.cit., Vol.4, p.583.

2. Wilhelmy's early work is discussed by E. Farber, 'Early Studies Concerning Time in Chemical Reactions', Chymia, 1961, 7, 141

3. Wilhelmy published his ideas on heat theory as Versuch einer mathematisch-physikalischen Wärme-Theorie, Heidelberg, 1851.

4. For example, Eilhard Mitscherlich (1794-1863) used polarimetry to study the change in direction of polarized light of saccharose in dilute acids.

5. Optical rotation of the plane of polarized light was studied by Jean-Baptiste Biot (1774-1862) over a period of almost twenty years. From 1833, he used it as a means for measuring the concentration of sugar in solution.

In his investigation of the inversion of sucrose to glucose and fructose, Wilhelmy employed a polarimeter containing a Soleil double plate which enabled him to follow the change with great ease.¹ He considered these changes as a general phenomenon, representative of a large number of similar reactions which were dependent on various factors such as concentration, temperature, nature and quantity of the acid. "However", he wrote, "this is certainly only one member of a greater series of phenomena which all follow general laws of nature".² To establish the laws governing the process of change, Wilhelmy considered that,

it will first be necessary to make one or the other assumption, to express the event by a mathematical formula and then to see whether this formula is consistent with the results of the experiments.

If dZ represents the loss of sugar in the time element dT , we assume that this loss is determined by the expression

$$\frac{-dZ}{dT} = MZS$$

where M is the average value of the infinitely small unit of sugar converted in the time element by the action of the amount of acid present.³

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1. L. Wilhelmy, Poggendorf's Ann., 1850, 81, 413-433, 499-526. Translated in part by H.M. Leicester, H.S. Klickstein, A Source Book in Chemistry, 1400-1900, New York, 1952, 396.
 2. ibid., 397.
 3. L. Wilhelmy, op.cit.

Z represented the amount of sugar, S that of the acid. By integration, he obtained the expression,

$$\log Z_1 = - \int_0^T MS \, dT \quad (1)$$

$$\log Z_1 = -MST + C \quad (2)$$

for $T = 0$, $z = Z_0$, so that

$$Z = Z_0 e^{-MST} \quad (3)$$

or

$$\log Z_0 - \log Z = MTS \quad (4)$$

The influence of time on the inversion was investigated by means of this equation, using a mixture of 10 grams of sugar and 2 grams of nitric acid. The relationship, (4), was found to hold, within limits. Wilhelmy applied the same formula to different systems, using both organic and mineral acids, including nitric, sulphuric, oxalic and phosphoric acids. Both phosphoric and acetic acids were found to react extremely slowly. Although the influence of factors such as concentration, temperature and the increase in volume were taken into account, Wilhelmy assumed that the temperature effect followed the same exponential law as the concentration. Despite the fact that he was dealing with a chemical reaction, the physical basis of Wilhelmy's reasoning is evident. For the temperature-free velocity coefficient, m , he derived the equation

$$m = k \beta^t (1 - \alpha t),$$

where $t = t^{\circ}\text{C}$, and k , β and α were constants.¹ Wilhelmy identified α with the coefficient of expansion of the liquid but this proved to be far too simple an approximation.

1. L. Wilhelmy, op.cit., 422, 499.

Wilhelmy's work is exceptionally interesting on several accounts, in addition to its pioneering nature. The origins of his chemical rate laws can be seen to have evolved directly by analogy with physical phenomenon. The exploration of chemical reactions using the familiar tools of physics, was, as yet, new territory. As well as establishing, for the first time, a quantified law of rate of chemical reaction, Wilhelmy was also breaking new ground in the development of chemical theory, a reversal of the traditional methods of chemical empiricism. His rate law was developed theoretically, on physical assumptions. The derivation of the equation

$$Z = Z_0 e^{-M_s T}$$

had then to be proved correct, or otherwise, by experimental testing.¹

By developing an exponential form of the equation, Wilhelmy was also able to deduce a general observation which finally made the time factor an integral part of chemical processes;

A necessary conclusion from the equation, moreover, is that when $T = \infty$, Z can become zero, hence the inversion of the sugar, strictly speaking, is never ended, although due to the smallness of the residue, very soon, a further decrease is not

1. This procedure has been taken to typify the development of physics. See later discussion.

noticeable.¹

Wilhelmy's work on the rates of chemical reaction remained unnoticed until Ostwald drew attention to it over thirty years later, in 1884.² In his book, L'Evolution d'une Science, Ostwald repeated his belief concerning the importance of Wilhelmy's contribution to chemistry in general - and to industrial chemistry in particular,

...il y a encore un intérêt pratique considérable à bien connaître les lois de la vitesse des réactions...il est important d'accélérer les réactions lentes autant que possible, car, pour l'industrie chimique comme pour toute autre, le temps, c'est de l'argent.³

Wilhelmy was also the first to employ the differential equation in following the course of a chemical reaction.⁴ Probably, the roots of this inspired choice lay in his earlier work on general properties of heat. Isomeric compounds of

1. L. Wilhelmy, op.cit., 399.

2. J. Prakt. Chem., 1884, XXIX, 385.

3. W. Ostwald, L'Evolution d'une Science, La Chimie, Paris, 1909, 260:

'...there is also an interesting practical consideration in knowing the laws for the rates of reaction...It is important to accelerate slow reactions as much as possible, because, for chemical industry, as in all others, time is money.'

4, See J.W. Mellor, Chemical Statics and Dynamics, London, 1904, 181.

equal specific gravity and equal boiling points, he thought, must have equal coefficients of expansion.¹ In this work, the change of specific heat with temperature was analysed by means of differential equations, following a tradition begun by Lambert seventy years earlier. Wilhelmy's heat theories extended to thermodynamics and the phenomena of heat movement, based upon the work of Robert Mayer on the equivalence of heat and work, published only a few years previously.

Although first and foremost a physicist (he founded the Physical Society in Berlin in 1845), Wilhelmy's novel approach to the understanding of natural phenomena appears not to have recognised any barrier between mathematical, physical and chemical processes. It was, to him, all part of a desire to "open up a complete understanding of the essence of natural forces", to which he had dedicated his major work, published in 1851.² It was an ambition not to be entirely fulfilled. In his method of chemical analysis it is not difficult to recognise the type of inter-disciplinary thinking which, in the hands of chemists like Ostwald and van't Hoff, became the new science of physical chemistry.

The utilization of familiar, existing models with which to explain, as yet, unexplored phenomena was not unique to Wilhelmy. In that very same year, 1850, Alexander

1. L. Wilhelmy, Versuch einer Mathematisch, op.cit., 1851.

2. L. Wilhelmy, op.cit.

Williamson was considering the dynamics of chemistry from another viewpoint, also employing old, well-established theories. The final establishment of the law of mass action, inspired by Berthollet, and touched upon by Wilhelmy, was to require the use of the physical model of balanced forces. In a somewhat different approach, the search for an understanding of the course of chemical change first required the recognition of chemical reactions as dynamic processes, which embody matter in motion, undergoing continuous change. This was to evolve from the development of the atomic theory of matter, involving controversies both ancient and contemporary and of fundamental importance to the theory of chemistry.

2.2. The Dynamic View of Chemistry: Matter, Motion, Change and Continuity

If the seventeenth and eighteenth centuries can be said to have been dominated by a Mechanical Philosophy, the century which followed can perhaps, equally and arguably, be described as one bound to a dynamic philosophy.¹ Two major scientific concepts which became inextricably associated with the 19th century intellectual milieu were the re-emergence of the idea of matter in motion and the evolution of the concept of energy. The century opened with a new atomic theory, debated the theory of evolution, developed a kinetic theory of gases and thermodynamics, saw the discovery of the electron - and in a strange sense, ended with the feeling of dissatisfaction which perhaps comes with all phenomena when sophistication takes over. John Theodore Merz, writing in that very era put it thus:

with their increasing complexity, modern dynamical explanations have undoubtedly, to every impartial observer, acquired a certain

1. J.T. Merz, A History of European Thought in the 19th Century, New York, 1965, Vol. II.

character of artificiality which suggests the question to what extent all such mechanical schemes are an expression of actual truths or merely useful illustrations....we are thus led beyond the province of scientific into that of philosophic thought....we (shall) frequently have occasion to note this tendency of the purely scientific thought of the century to lead up to philosophical problems. Wherever this is the case, a history of scientific thought may legitimately close one of its chapters.¹

The concepts of dynamics and motion, as we have seen, are associated with the notion of time as well as matter.² From a physical point of view at least, the properties of matter, motion and the element of time were fairly well developed by the beginning of the 19th century; light, it was thought, consisted of something in motion (whether it was corpuscular or periodic) and light took time to travel

1. J.T. Merz, op. cit., 199.

2. For an interesting account of the role of time in the 19th century, see J.H. Buckley, The Triumph of Time, Cambridge, Mass., 1967.

from one point in space to another. Fizeau's measurement of the velocity of light, around the middle of the century, helped to unite theories of matter, motion and space. Nevertheless, the problems, hypothesis and subsequent debates on the dynamic view of nature still held peripatetic echoes, which, not infrequently, only served to confuse and intensify the dilemma. The conflict of how to explain the apparent rest and permanency of objects, as they appeared to the human senses, in terms of continuous motion, stretches into antiquity. On the macro-scale, the movement of the earth was a controversy which had dominated the very beginnings of astronomical science in Europe. From the 15th century onwards, figures like Nicholas of Cusa and da Vinci had advanced the ideas of motion to an unprecedented level.¹

At the other end of the scale, the familiar questions pertained to the atoms of matter. Although chemists and physicists alike had inherited the same schools of thoughts in philosophy, the direction of their developments by the 19th century had resulted in very divergent paths. Theories of

1. Interestingly, early ideas in motion, continuity and (subsequent) relativity indicated highly sophisticated associations between discreteness and numbers, and that of continuity with geometry: see for example, H.T. Pledge, Science since 1500, London, 1939; W.C. Dampier, A History of Science, Cambridge, 1929.

matter, especially for the chemist,¹ continued to ferment only gently after Dalton's theory of 1801.² Generally speaking, the view of fundamental matter at the beginning of the 19th century was largely corpuscular, dominated as it was, still, by the spirit of Newton. This picture, though not sharply in focus, was at least a fairly confident one. The era of debate lay yet ahead. In 1802, Humphry Davy wrote calmly enough:

The different bodies in nature are composed of particles or minute parts, individually imperceptible to the senses. When the particles are similar, the bodies they constitute are denominated simple, and when they are dissimilar, compound. The chemical phenomena result from the different arrangement of the particles of bodies; and the powers that produce these arrangements are repulsion, or the agency of heat, and attraction.³

1. The term 'chemist', designating those practising chemistry as a profession, did not become formalised in Britain until the 1870's. See C.A. Russell, G.K. Roberts, N. Coley, Chemists by Profession, Open University Press, 1977. In the present work, the term chemist will imply those actively pursuing chemistry, professionally or otherwise.

2. On the background to Dalton and the Atomic Theory, see: John Dalton and the Progress of Science, ed. by D.S.L. Cardwell, Manchester, 1968.

3. H. Davy, Syllabus of a Course of Lectures at the Royal Institution, London, 1802.

In keeping with many writings of that period, authors of articles on the nature of matter very often did not define precisely what they meant by the term 'particles'. These 'simple' or 'compound' particles mentioned by Davy may have referred to, but were not necessarily identical with, the chemical elements as defined by Lavoisier, for example, as substances which resisted further chemical analysis.

In retrospect, part of the difficulty in understanding the fundamental nature of matter appears to have stemmed from a singular lack of clarity in definition, semantic in origin, rather than scientific; a breakdown of communications as to what was precisely intended.¹ These problems finally gave rise, in the second half of 19th century Britain, to a series of firm and persistent chemical 'Atomic Debates'.² Frequently bordering on the passionate, these debates were to extend into the early years of the present century.

2.2.1 Matter and Motion: The Ideas of Alexander Williamson

Amongst those who played an eminent role in the controversies was Alexander Williamson, who, in 1869, was President

1. For an interesting account of the Atom, as understood in mid-19th century, see J.C. Maxwell's article in Encyclopaedia Britannica, 1875, Vol.3, 36-49.

2. See W.H. Brock, D.M. Knight, 'The Atomic Debate', ISIS, 1965, 56, 5-25; The Atomic Debates, ed. by W.H. Brock, Leicester University Press, 1967; D.M. Knight, Atoms and Elements, London, 1967.

of the Chemical Society. His paper of that year, 'On the Atomic Theory' is particularly interesting, for reasons beyond merely putting forward forcefully his ideas on atomism; it seems to indicate a kind of dogmatic lethargy into which chemists appeared to have lapsed over the apparent confusion presented by the matter theory. Frustrated perhaps by the desultory arguments, it was, nevertheless, a state which many of those working in the chemical disciplines deplored.¹ As the chemist Edmund J. Mills put it:

I address myself more especially to chemists; and their science is at the present time, and at this instant to the judicial reader, in the very crisis when the adoption of a real criterion is of the supremest consequence. Sad in the poverty of symbolic resources, miserably unreasoned and deficient in power, it urgently requires an entire reform of its prevailing theory.²

More specifically, referring to the Atomic Theory, Williamson wrote:

It certainly does seem strange that men accustomed to consult nature by experiments so constantly as chemists do, should make use of a system of ideas of which such (that is, skeptical) things can be said. I think

1. For other views at the time on Matter Theory, see: William Crookes, Presidential Address, B.A. Reports, 1866, 558-76; A. Kekulé, The Laboratory, 1867, 1, 303.

2. Phil. Mag., 1873, (4th Series), 46, 398.

I am not overstating the fact, when I say that, on the one hand, all chemists use the Atomic Theory, and that on the other hand, a considerable number of them view it with mistrust, some with positive dislike.¹

Williamson, who was born in London in 1824, has been called "the most influential chemist in Great Britain during the period 1850-1870".² Certainly, his life and work has inspired an appreciable number of studies in recent times.³ Yet Williamson's reputation, as far as active research was concerned, was relatively short-lived. In fact, it is largely based on his etherification studies, which were published over a period of only four years, and were virtually complete by 1854.

Williamson's work on the ethers was, however, not merely a series of chemical syntheses. It contained original conjectures on the ideas of atoms in motion and dynamic equilibrium which were to have far-reaching consequences. These hypotheses were made surprisingly early, considering the debate on the very existence of atoms still lay ahead. His specific

1. A.W. Williamson, J.Chem.Soc., 1869, 22, 328.

2. Dic. of Sci.Biography, Vol.14, 394-396.

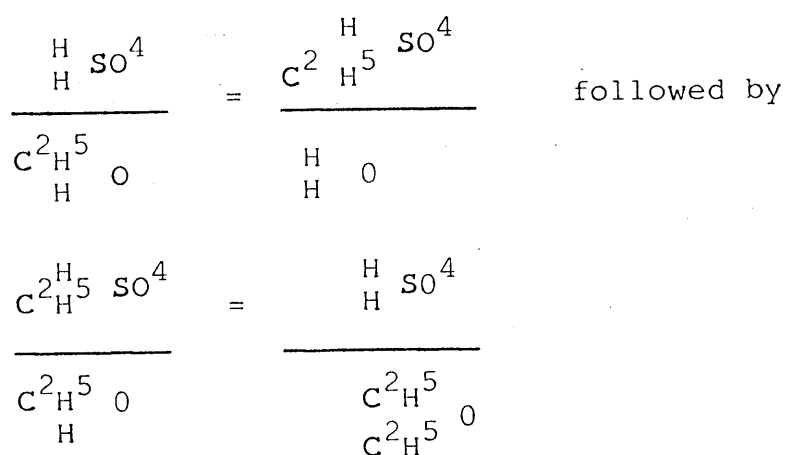
3. See: E.R. Paul, "Alexander Williamson on the Atomic Theory", Ann. Sci., 1978, 35, 17; J.Harris, W.H.Brock, "From Giessen to Gower Street, towards a Biography of Alexander Williamson", Ann.Sci., 1974, 31,95; J.Harris, The Work of Williamson and its Relation to the Type Theory of Wurtz, M.Sc.Thesis,London,1926; J.S.Lungley "The Life and Chemical Investigations of A.W.Williamson (1824-1904)": Part II Chemistry Thesis, Oxford, 1964.

reference to the time factor in chemical theory was only one of several new ideas which he introduced in the process of his work on ether synthesis.

Williamson's paper on the theory of etherification was read before the British Association for the Advancement of Science at Edinburgh in 1850.¹ In it, Williamson described his experiments on the etherification of ethyl alcohol by sulphuric acid, with sulphovinic acid and water as intermediates. The reasoning behind his idea of molecules transposing positions during the reaction is expressed with great clarity:

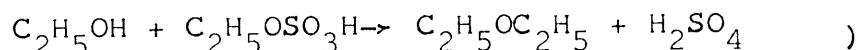
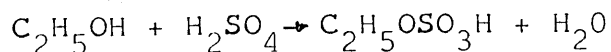
the simplest mode is, at the same time, the one most free from hypothesis; it consists in stating the fact, that sulphuric acid and alcohol are transformed into sulphovinic acid and water, by half the hydrogen of the former changing places with the carburetted hydrogen of the latter.²

In his terminology:



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1. A.W. Williamson, Papers on Etherification and on the Constitution of Salts, Alembic Club Reprints, Edinburgh, 1949; Phil. Mag., 1850, 37, 350.
 2. Phil. Mag., 1850, 37, 350.

(This is quite close to the equation as might now be written:



He continues:

The sulphuric acid thus reproduced comes again in contact with alcohol, forming sulphovinic acid, which reacts as before; and so the process goes on continuously, as found in practice. We thus see that the formation of aether from alcohol is neither a process of simple separation, nor one of mere synthesis; but that it consists in the substitution of one molecule for another, and is effected by double decomposition between two compounds.....for one-sixth of the H in alcohol truly exhibits different reactions from the remaining five and must therefore be contained in that compound in a different manner from them.¹

At the time of these experiments, various theories existed for the formulae of ether and alcohol:- as oxides of the type $(\text{C}_4\text{H}_5)\text{O}, \text{C}_2\text{H}_3\text{O}$; or as hydrates of the radical C_4H_4 giving $\text{C}_4\text{H}_4\text{H}_2\text{O}$ and $2\text{C}_4\text{H}_4 \cdot \text{H}_2\text{O}$. The most prevalent theory at the time of Williamson's investigations was that alcohol, $\text{C}_4\text{H}_5 \cdot \text{H}_2\text{O}$ was a hydrate of ether, $\text{C}_4\text{H}_5\text{O}$.²

1. Phil. Mag., 1850, 37, 354.

2. See for example J.R. Partington, A History of Chemistry, London, 1964, Vol. 4, 445.

Williamson, however, suggested that the process of etherification occurred by the catalytic or contact action of sulphuric acid. At the same time he introduced the idea of the chemical reaction as taking place in different stages: the substitution of an atom of one reagent by a group or radical from another reagent, forming an intermediary which then proceeds to the completion of the reaction. And he concluded that the ease of the substitution distinguished one of the H atoms in the alcohol from the others, an idea which led him to visualize chemical equilibrium, not as a static state, but as a condition of continuous flux. His method of reasoning, even more than a century later, appears exceptionally logical:

Before quitting the subject of etherification, I would wish to add a few words on an application which, naturally enough, suggests itself of the fact to which the process is here ascribed. I refer to the transfer of homologous molecules in alternately opposite directions which as I have endeavoured to show, is the cause of the continuous action of sulphuric acid in this remarkable process. It may naturally be asked, why do hydrogen and carburetted hydrogen thus continuously change places?.....Now, in reflecting upon this remarkable fact, it strikes the mind at once that the facility of interchange must be greater the more close the analogy between the molecules exchanged: that if hydrogen and amyle can replace one another in a compound, hydrogen and aether

which are more nearly allied in composition and properties, must be able to replace one another more easily in the same compound if this be true, must not the exchange of one molecule for another of identical properties be the most easily effected of all?¹

Williamson's analysis thus introduces a picture of chemical reaction as a dynamic and continuous process, far from the familiar, one step reactants/products phenomenon considered as constituting chemical change. He continued:

We are thus forced to admit, that in an aggregate of molecules of any compound, there is an exchange constantly going on between the elements which are contained in it.....in using the atomic theory, chemists have added to it of late years an unsafe and, as I think, an unwarrantable hypothesis, namely that the atoms are in a state of rest. Now this hypothesis I discard, and reason upon the broader basis of atomic motion.²

These extracts illustrate well Williamson's direct approach to what was a revolutionary and new chemical hypothesis, that of dynamic equilibrium. It was not unexpected then, that of his chemical contemporaries, few who seriously considered his ideas would not have had cause to suffer mental digestion problems in the initial stages.

1. A.W. Williamson, Quart. J. Chem. Soc., 1852, 4, 229.

2. ibid.

His next paper, Suggestions for the Dynamics of Chemistry derived from the theory of Etherification, established his dynamic view of chemical processes on a much fuller basis.¹ In order to accept this new chemical 'mechanism', it was first necessary, undoubtedly, to disengage the minds of the chemists of the day from pre-conceived notions on the subject. This 'mental barrier' was probably considerable. In the first place, the question of mere existence of atoms as the actual entities taking part in chemical reactions had not, as yet, been satisfactorily established. The idea of chemical atoms undergoing continuous exchange during reactions must therefore have lain beyond the average sensibility. Secondly, even for those who accepted atomism in the mid-19th century, it was generally considered that the key to why chemical reactions occurred in a specific way still centred around a search for the elusive affinity forces.

Williamson was well aware of this and repeated:

The atomic theory has hitherto been tacitly connected with an unsafe and unjustifiable hypothesis, namely, that the atoms are in a state of rest; the dynamics of chemistry will commence with the rejection of this supposition and will study the degree and kind of motion which atoms possess, and reduce to this one fact the various

1. Notices of the Proceedings at the Meetings of the Members of the Roy. Inst., 1851-54, Vol.1, 90-94: reprinted in The Alembic Club Reprint, Cl9, 1949.

phenomenon of change, which are now
attributed to occult forces.¹

In fact, it is all too tempting to see in many of Williamson's statements an air of prognostication, which was probably not intended. Did his statement, for instance, that:

chemical science has proved the indestructibility of matter, but it has yet to prove the indestructibility of motion or momentum by showing its transfer and dispersion among atoms.²

imply an early intuitive understanding of a relation between matter and energy? Possibly not. But certainly his paper puts forward, very convincingly, the idea that Williamson, whilst propounding theories of reaction 'mechanism' for etherification, touched very closely on the relationship between rates of reaction, the time factor in chemical processes, and the quantity of reactants present. For he wrote:

The exchange of analogous particles actually constitutes double decomposition; and its occurrence in alternately opposite directions causes the two substances used to alternate with the two other compounds formed by the exchange of their basis; so that in such a mixture, four substances are constantly to be found, the quantity of each substance corresponding to the average number of atoms which, in each moment of time, are in that state of combination.....the quantity of the products of this interchange remains

1. A.W. Williamson, Papers on Etherification, op.cit., 18-24.

2. A.W. Williamson, op.cit. 18-24.

constant, because a similar double decomposition, equal in absolute number of atoms per unit of time, is constantly going on between these products, re-producing the original compounds.¹

Williamson actually equated chemical force to the quantity of substances taking part in double decompositions. In the conclusion of his paper, he wrote:

On the mixture of equivalent proportions of a couple of salts in aqueous solution, a certain amount of decomposition ensues, forming two other salts, and the chemical force may be considered proportional to the quantity of one couple compared to that of the other. Now, as the proportion is only kept up by the number of exchanges in the one direction being absolutely the same in each moment of time as those in the opposite direction, it is clear that the relative velocity of interchange must be greatest between the elements of the couple of which the quantity is least; and chemical force must be inversely proportional to the velocity of these interchanges.²

Interestingly, Williamson does not use the term affinity but chemical force, and relates this to velocity. This idea is

1. Papers on Etherification, op.cit. 23.
2. On Etherification, op.cit., 23.

particularly revealing in view of later developments in chemical reaction rates, when motion, change and continuity in chemical processes become, for the first time, ideas capable of quantified expression.

But in 1850, the idea of quantified time factors in chemical change was still some distance away, despite the obvious relevance of Williamson's work. The search for time factors in science is essentially a seeking after of an understanding of the order of nature and its laws, a natural process of scientific development. History shows that this development occurs, for different disciplines, at different periods and sometimes, as it appears in the case of Williamson's hypothesis, out of sequence with logical progress.

Even further removed than the idea of time and chemical change was the concept of spatial atoms, a concept which, though far removed from pure abstraction, was still a very distant point on the horizon.¹ Williamson began his paper of 1851 with the fateful words:

1. On the development of stereo-atoms see: Foundations of Stereo-chemistry, Memoires of Pasteur, van't Hoff, le Bel and Wisliscenus, trans. and ed. by G.M. Richardson, N.York, 1901; J.H. van't Hoff, "Sur les Formules de Structure dans l'Espace", Arch. Neerland.des Sci.Exactes et Nat., 1874,9,445-454; J.A.le Bel "Sur les relations qui existent entre les formules atomiques des corps organiques", Bull.de la Soc.Chimique de France, 1874, 2,2,337-347: Reprinted in Classics in the Theory of Chemical Combination, ed. by O.T. Benfey, New York, 1963.

the human mind is only capable of understanding complicated phenomena when prepared by the study of simpler ones; and one of the most remarkable illustrations of this necessary order is afforded by the preparation of dynamical laws, by the consideration of statical facts. In statics we consider phenomena in a state of rest, while in dynamics we study their change; and this distinction has been concisely stated by saying that the transition from the statical to the dynamical point of view, consists in super-adding the consideration of time to that of space.....there are prima facie evidences that time is necessary for chemical action;- but this fact, although it has been noticed, has not yet entered into the explanation of phenomena.¹

Williamson does not stipulate when or by whom this time factor had previously been observed in chemical phenomena. But does his statement give, perhaps unwittingly, an accurate description of what distinguished the development of chemical theory from those of physics up to his era? - a difference of traditions which had its roots in the very earliest associations between chemistry with occult forces and physics with the motion of the Heavenly Bodies? Was the habit for

1. Notices of the Proc. of Members of Roy. Inst. op.cit.,
90-94

chemists to work only from the empirical so deeply ingrained that to diverge from this was to guarantee confusion and regression into metaphysics? was it a necessary criterion for those seeking chemical understanding to grasp only those facts which supported existing notions, ignoring others which appeared contradictory? These developments are not uncommon. Were chemists more guilty of this than most?

Williamson obviously thought this and said so:

.....we only seek and see those facts which are more or less connected with our theoretical notions, and in most cases shut our eyes to such cases as appear contrary to them. This is peculiarly the case with chemical theory and chemical facts at the present day.....in fact it is certain that if we could sufficiently disengage our minds from preconceived notions on the subject, we should view these substances, which, by more or less troublesome processes we separate out from the bodies presented to us by nature, rather as exceptional and artificial products, than as the most normal and natural.¹

The physicists of the day were not slow to notice this particular chemical malaise. In the controversy which was to follow on the reality of atoms, it was the physicists who most supported Williamson's views and found them convincing. The arguments of the anti-atomists, erudite as they were, for

1. Notices of the Proc. of Members of Roy.Inst. op.cit., 90-94.

example in the papers of Edmund Mills, were somewhat less so. Frequently self-contradictory, the opponents of atomism caused Williamson to comment caustically that when one of these skeptics,

has ascertained by analysis the percentage composition of a compound, and wants to find its formula, he divides the percentage weight of each element by its atomic weight. He seeks for the smallest integral numbers which represent the proportion of atoms.... He looks to the reaction of the body for aid in constructing his atomic formula and controls his analyses by considerations derived from well established reactions.....In no case does he reason on a basis independent of the atomic theory.¹

Despite his strong convictions and the opinions expressed in his earlier work, Williamson was forced, nevertheless, to confess to an incomplete understanding of the problem of atoms; just how 'elementary' were Dalton's atoms? - after his bold and extremely far-sighted hypothesis on the theory of etherification, Williamson's concluding remarks on the Atomic Theory were not encouraging for the development of a unified chemical theory of matter:

1. J.Chem.Soc., 1869, 22, 340.

In using the atomic language and atomic ideas, it seems to me of great importance that we should limit our words as much as possible to statements of facts, and put aside into the realm of imagination all that is not in evidence. Thus the question whether our elementary atoms are in their nature indivisible, or whether they are built up of smaller particles, is one upon which I, as a chemist, have no hold whatever, and I may say that in chemistry the question is not raised by any evidence whatsoever.¹

These thoughts were shared and echoed by many pro-atomists of the day. Only two years previously, Kekulé had expressed similar views very pointedly and simply:

The question whether atoms exist or not has but little significance in a chemical point of view; its discussion belongs rather to metaphysics. In chemistry we have only to decide whether the assumption of atoms is an hypothesis adaptable to the explanation of chemical phenomena.²

Kekulé saw the importance of developing the atomic theory, not as an end in itself but rather as something essential in order to advance the knowledge of the 'mechanism of

1. J.Chem.Soc., 1869, 22, 365.

2. A. Kekulé, The Laboratory, 1867, 1, 304.

chemical phenomena'. His classical papers on the chain-forming capacity of carbon atoms, published almost a decade earlier, had already established the importance of this aspect of chemical change.¹ Kekulé advocated a dynamic view of matter,² though he clearly adhered still to a theory of chemical affinity:

When two molecules react, they first attract each other by virtue of their chemical affinity and align themselves next to each other. The affinities of the individual atoms then cause atoms which previously belonged to different molecules to come

1. A. Kekulé, Ann. Chem., 1858, 106, 137.

2. In 1872, Kekulé was to re-iterate his belief in this dynamic view of matter. He wrote "the valency is the relative number of impulses which one atom experiences from another atom in unit time. In the same time in which the monovalent atoms rebound together in a diatomic molecule, given equal temperature, divalent atoms in a diatomic molecule likewise come twice into collision."; F.A. Kekulé, Annalen, 1872, 162, 87.

The problem of 'bonds' or affinity between atoms was, at the time, a vitally important one, and in some ways, of more significance to the immediate understanding of chemical phenomenon than the idea of dynamic chemistry. For an account of the development of chemical bonding see: C.A. Russell, The History of Valency, Leicester Univ. Press, 1971.

into intimate contact. For that reason, the group that was divided in one direction prior to reaction, now falls apart in another direction.¹

The mechanism suggested by Kekulé is particularly interesting and relevant to the present thesis because, like Williamson's hypothesis, it demanded a closer examination of the process by which chemical changes evolve. Though still lacking a detailed analysis of quantified factors involved in the process of change, the implications of Kekulé's 'mechanism' were to have far-reaching consequences in the understanding of the structure of chemistry.² Of special significance in the evolution of the concept of reaction mechanism was the suggestion by Kekulé of an intermediate state (Zwischenstadium) formed during the chemical change; not only so, but that this 'molecular aggregate can be retained, and by deliberate changes in the conditions, the decomposition can be brought to completion'.³ The idea of intermediate stages occurring during a chemical reaction was an important step in the elucidation of the course of chemical change, as we shall see.

But to return to Kekulé's theories on the reality of atoms, we find his words relevant indeed, both for the protagonists in the subsequent atomic debates and also for its truth, as it was to emerge in a later period:

1. A. Kekulé, Ann.Chem., 1858, 106, 137.

2. For an interesting account of this and other related chemical developments, see: The Structure of Chemistry by C.A. Russell, Units 1-3 in course S304, The Open University, 1976.

3. A. Kekulé, Ann. Chem. 1858, 106, 137.

I have no hesitation in saying that, from a philosophical point of view, I do not believe in the actual existence of atoms, taking the word in its literal significance of indivisible particles of matter. I rather expect that we shall some day find, for what we now call atoms, a mathematico—mechanical explanation.....As a chemist,..I regard the assumption of atoms not only as advisable, but as absolutely necessary in chemistry. I will even go further, and declare my belief that chemical atoms exist, provided the term be understood to denote those particles of matter which undergo no further division in chemical metamorphoses.¹

Kekulé goes on to elaborate his views, that even were a theory of the constitution of atoms to emerge - important as such a knowledge might be for the general philosophy of matter, it would make but little alteration in chemistry. The chemical atom would always remain the chemical unit. These beliefs appear, in Kekulé's writing, extremely well formulated, and even a century later, to be convincing. Certainly, it stands in marked contrast to the more passionate, sometimes histrionic speeches of some of the chemists taking part in the atomic debates two years later. Indeed, Williamson

1. A. Kekulé, The Laboratory, op.cit., 304.

also expressed his arguments in a very similar vein, yet, perhaps without producing equal impact:

whether the particles of matter have a spherical form or not, whether they are in their nature indivisible, whether they are in reality the ultimate atoms of matter,

he knew not nor did such questions exist for him as a chemist.¹

2.2.2. Change and Continuity: the ideas of Edmund J. Mills

As an event which certainly appears to have aroused the chemical community in Britain out of some of its apparent apathy, the occasion of the first atomic debate proved to be 'a memorable and interesting evening in the life of the Chemical Society'.² Among the participants present were many leading chemical figures of the day; apart from Williamson, also attending were Sir Benjamin Brodie, Edward Frankland, William Odling, George Carey Foster and Edmund J. Mills. The last of these, Edmund Mills, presented what was probably the most passionate anti-atomistic views of those present and was to sustain this approach over a period of almost a decade.³

In a series of papers, beginning in 1867, Mills put forward his ideas on atoms, matter, motion and continuity,

1. J.Chem.Soc., 1869, 22, 434.

2. E. Divers, Proc.Roy.Soc., 1907, 78A, xli.

3. Edmund James Mills, 1840-1921, became Professor of Technical Chemistry at Anderson's College, Glasgow.

in words which contained more than overtones of the metaphysical. His paper, "The Atomic Theory", was the third in the series, and did not appear until 1871.¹ His thesis, that motion was the sole reliable guide in this scientific debate was, by then, well known to his readers. Mills rejected Dalton's theory of atoms, because he believed the latter to have regarded 'atoms as enjoying perfect repose, unless when mechanically or chemically disturbed.'² It seems doubtful whether Dalton himself really intended such a view. But in this fairly lengthy memoir, although Mills does not mention Williamson specifically by name, it was the idea of a dynamic theory of atoms, proposed over twenty years earlier, which was foremost in Mills' mind for he wrote:

...atoms have been considered from another point of view. It has been found by not a few thinkers that rest is a condition which falsely represents the facts of nature, and that atoms must therefore be conceived as moving with an industry to which cessation is unknown.³

The foundations of Mills' arguments on what he termed 'the impossibility of the finite and discrete' can be traced without much difficulty to philosophic theories prevalent in the 19th century. The germinal ideas of Hobbes and Hegel are not heavily disguised in his objections to the atomic theory and Mills' thesis soon becomes a somewhat polemical

1. E.J. Mills, Phil.Mag., 1871 (4th Series), 42, 112.

2. ibid., 113.

3. ibid.

discussion on the properties of the real and unreal. "But", wrote Mills, "if all chemical substances consist of atoms, and position is possible without them, how can such position be known or determined?"¹

Mills, following Hegel's philosophy, believed that pure being indicated pure nothing. This, he said, implied that pure position could also be assigned to the same category.² And Mills wrote, not without a note of triumph, "determinate space or position, with the only thing that can determine it taken away, is contradiction itself."³ Although some of Mills' arguments seem totally fallacious, his words were not entirely without foundation. Closely associated with the ideas of atoms at the time were theories on how these atoms were joined together, or separated, in an overall picture of chemical constitution, a picture which was by no means clear or easily understood. These were the 'units of affinity' or valency problems which in 1871, still remained largely unresolved. Mills quotes Kekulé's work at some length and concludes from this that,

It is assumed that substances consist of molecules, these again of atoms; that determinate space or position (stelle) is conceivable without atoms, and exists indeed in their absence; and that into this space there stretch at all times mysterious units of affinity, which, when the atoms are no longer present, strive after combination.⁴

1. See reference 2 below.

2. E.J. Mills, Phil. Mag., 1871, (4th Series), 42, 117.

3. ibid.

4. ibid., 117.

His reasoning is not entirely clear, since the arguments were certainly not what Kekulé would have intended. Elsewhere, Mills' contention, that quantity does not consist of indivisibles, is reminiscent of the kind of polemics to which van Helmont referred in our earlier discussion on time. Indeed, it is apparent that much of what has been said about the divisibility or finiteness of matter is equally applicable to the paradox of time, had such ideas occurred to Mills.

Although Mills' tendency towards pure abstraction caused him to be dismissed as a meta-physician¹, his arguments may, nevertheless, deserve a closer examination. For if Mills' reasons for writing his extended essays, On Statical and Dynamical Ideas in Chemistry, which appeared in four parts,² were to take a broad overview of the most fundamental principles on which chemistry was then based, and place them in the wider context of a universal philosophy, then perhaps some credit is due to him. Traditionally, it has always been assumed and accepted that chemistry is, inherently, an eminently practical subject. Does chemistry then have a philosophic basis in the light of this assumption? This is a question which relates to the earlier discussion on the fundamental theories of time. It is a question which, in the process of developing theories for the course of chemical change, we will have cause to remember.

1. See Chem. News, 1876, 32, 62.

2. Part I: Phil. Mag., 1869, (4th S.), 37, 461; Part II: ibid, 1870, (4th Ser.), 40, 259; Part III: ibid, 1871, (4th S.), 42, 112; Part IV: ibid, 1873, (4th Ser.), 46, 398.

It is no exaggeration to say that both the dynamic ideas envisaged by Williamson, and those relating to the rates of chemical change sought by Harcourt, which will be discussed later, required this broader outlook, and called for visions beyond the purely practical. By all accounts, Mills' unconventional views had little impact on his chemical contemporaries,¹ who needed the convenience of atoms, units of affinity, and any other theory which could help them overcome problems in what was, without a doubt, an intractable discipline.

Central to Mills' arguments, however, remained the rejection of any idea of atomism, in matter or space, and an unshakeable conviction of the importance of a dynamic chemistry. "On close examination", as he put it, "it is found that the substratum (of the atomic theory) has its necessity only in the imagination.....surrounded on all sides with continuity, motion, and change, our most popular ideas relate to limits, repose, and stability".² Taking a positivist view of the matter, he continued:

For who has ever seen that which he cannot divide? or who, being unable to divide, would not at once suspect a defect in his tools rather than indivisibility in the substance submitted to experiment? The experience of two thousand years has failed to produce or to discover a single atom of the innumerable millions that have existed

1. See The Atomic Debates, ed. by W.H. Brock, Leicester Univ. Press, 1967.

2. E.J. Mills, op.cit., 1871, 123

during the whole of that time....¹

Mills chose to compare the atomic theory with the earlier phlogiston period, an unfortunate choice for him, since time had proved the latter false, but for the atom, a new era was just beginning. Less than thirty years after Mills' vehement denial of its existence, the new atomic age was just dawning, beginning with Thomson's discovery of the electron. But for Mills, finally and irrevocably, the atomic theory had no experimental basis, was untrue to nature generally, and consisted in the main, of a materialistic fallacy; whilst in contrast, Mills thought, the idea of motion, with its subordinate laws, true both to nature and life, remained,

the highest product of the scientific and the
pure reason, and the noblest generalization
the world has yet known, because it is the only
one that neither limits nor enslaves.²

Mills' paper raises several interesting points, apart from painting an extremely vivid picture of how strong was the opposition in the atomic theory debate at the time. In his fundamental argument, that atoms, as entities ⁱⁿ capable of division, do not truly exist, he approached modern theories of matter far closer than the pro-atomists of the day. On present theory, it is thought that the number of sub-atomic particles may be infinite in number, temporarily hidden only by the limited sources of power currently at our disposal. This view was, of course, shared by many others, even before

1. E.J. Mills, op.cit., 1871, 123.

2. ibid., 129.

Mills took his stand in the 19th century, as he pointed out. Thus, in quoting, he observed that Newton allowed of indivisibility only so far as ordinary or natural forces were concerned. Elsewhere, in a passage too often overlooked, Newton limited the indivisibility of matter to his own time - "But whether these parts, distinct and as yet undivided by natural forces, are able to be divided and sundered in their turn is uncertain" - and furthermore, Newton had allowed that space was divisible in infinitum.¹ In Descartes too, Mills sees a defender of his own views, for the French philosopher had regarded atoms - that is to say, parts of bodies or matter which are by nature indivisible - as being extended, no matter how small, and therefore all capable of division into smaller parts.²

Historically, this is a familiar situation: two opposing ideas, each proved to be correct in turn, at each stage creating a new scientific 'discovery', validated by the passing of time.³ This element of uncertainty in all scientific 'laws' was known and accepted in Mills' time. Liebig, for instance, writing in 1867, though not debating about matter theory specifically, had remarked:

we find that at all times the opinion obtained, that the conceptions were in harmony with the facts, and indeed the

1. E.J. Mills, op.cit., 1871, 126.

2. ibid.

3. Berthollet too, defeated in his theory of variable composition by Prout, has had his ideas reinstated, since the discovery of berthollides such as $\text{Fe}_{0.94}^0, \text{Fe}_{0.84}^0$

definitions always corresponded with the logical laws, but the later are always in opposition to the earlier; what had been held to be right is found to be wrong at a later period and thus the subsequent definitions annul the former ones, hence it becomes evident that the truth of the definitions does not depend upon the principles of logic alone.¹

To some degree then, Mills' ideas have been vindicated, as were those of his opponents in an earlier stage of development. Nevertheless, Mills, whether merely a champion of metaphysics, or supremely far-sighted, was unable to satisfy his own criterion of progress - rejecting the laws of atomism, he failed to define clearly his own theories of matter, what it was that actually demonstrated 'continuity, motion and change'. Pure motion may belong to the realm of pure metaphysics, but discreteness and continuity still demanded a concrete law of matter. In 1876, Mills very neatly predicted the fate of his own beliefs, in taking the first principle of science to be: that which is first in the order of nature is last in the order of knowledge. All science, Mills wrote, advances by going, in a sense, backwards, or at least by coming around; and the apotheosis and final triumph of human reason would be when, having

1. J. von Liebig, "On the Development of Ideas in Natural Philosophy", Chemical News, 1867, 252.

traversed the whole cycle of thought, it returns, 'enriched only with a deeper insight and a clearer consciousness'.¹

Meanwhile, in the autumn of 1869, the debate amongst British chemists raged on, and something bordering on a chemical showdown was in the air, or rather, on the floor of the Chemical Society's debating chamber at Burlington House. The occasion was, it appears, one of all or nothing: for either one 'accepted atomism because one believed atoms existed, or one rejected atoms completely. There was no room for utilitarian compromise or for the Comtean claim that the atomic hypothesis was a useful and logical artifice'.² Two papers of that year came closer to uniting the chemical dilemma with the metaphysical, an element so strongly apparent in Mills' arguments.

Both sides are correct. The atoms are the ultimate form of matter as we know it, in the form of the chemical elements. But no-one can affirm, or would think of doing so, that these elements are positively the ultimate forms of matter itself. On the other hand, there is the genuine feeling, justified by the remarkable relations between the atomic weights and the properties of the elements that they are probably compounds of yet simpler forms of matter, though their decomposition may not be possible to man.³

1. E.J. Mills, Phil. Mag., 1876 (5th Series), 1,1.

2. See The Atomic Debate, op. cit.

3. Chem. News, 1869, 20, 272.

In that same year, 1869, George C. Foster offered another view of chemical change which also held reconciliatory overtones: between the bodies which disappear, and those which appear, there existed certain relations, both quantitative and qualitative, so that the total mass under-going change remains constant. It may be, Foster thought, that in the process of this change, one portion of matter actually transmutes into another; that it ceases to exist as such, but is replaced by something else. If such changes were to occur, then, though the idea of atoms would not necessarily follow, from the reasoning which was most logical, Foster considered that an atomic hypothesis or basis was inevitable.¹ This interpretation of the problem holds more than a suggestion of physical-chemico insight, which, in the end was necessary to advance matter theory. Interestingly, this dual view - of a chemical phenomenon embodying physical changes - may have resulted from Foster's training in both disciplines, initially as a chemistry student of Williamson's before turning to physics.

The debate, uncertainty, and counter-debates over the reality of atoms were to continue well into the present century, beyond the discovery of the electron in 1897. Curiously, a dynamic theory of chemistry was used by Ostwald as recently as 1904 to demonstrate the obsolescence of any form of atomic theory. Even more curiously perhaps, many chemists were to initiate vital steps in the understanding of chemical processes without fully comprehending the nature of the building

1. J.Chem.Soc., 1869, 22, 438.

matter on which their chemistry was based. This is true, for example in the case of the development of rate studies by Harcourt. Although, as President of the Chemical Society during part of the Debate period, he could not have avoided the pervading contradictions and conflicts, he does not appear to have been perturbed by the lack of a concrete matter theory..

It is difficult to define precisely the ultimate solution of the atomic dilemma for chemists. Even in the first decade of the present century, there was a feeling that,

chemists remain not much less divided on the subject now than they were then.¹

Meanwhile, returning to the scene of chemical progress in the second half of the 19th century, as painted by contemporaries Edmund Mills and Alexander Williamson, it seems strange to discover that, despite their opposing stand on atomism, many of their arguments were founded on a similar thesis: their deep conviction that all Nature was dynamic, and that motion was the essence of all phenomena. Williamson had already, in 1850, expressed his ideas on dynamic chemistry. Some years later, Mills was to write,

the criterion (of scientific progress) at present required is attained in the idea of motion, such motion being understood of

1. Proc.Roy.Soc., 1907, 78A, xli.

itself.....without reference to anything
moved.¹

To this theme, contained in his On Statical and Dynamic Ideas in Chemistry, Mills was to return repeatedly.² Tachenius, the iatro-chemist, is credited by Mills with one of the first dynamic theories of chemistry, as well as being the originator of the idea that all salts are decomposable into acid and alkali. If, thought Mills, no satisfactory progress in understanding acid/base reactions had been made since those early days, it was surely because:

.....we attempt to carry out in practice a
statical definition on a dynamical under-
standing.³

Extending his dynamical ideas to chemical reactions and chemical functions, Mills stringently avoids the use of familiar expressions such as 'atom of matter', preferring instead to describe them as 'substances':

.....it is evident and not an uncommon
statement that we can only judge of a
substance by its reactions - that is
by motion. But if so, the statical
argument is abandoned and we can neither
continue to ascribe discrete parts to
chemical substances nor implicate them
in its formulae.⁴

1. E.J. Mills, Phil. Mag., 1869, (4th S), 37, 461.

2. ibid.

3. ibid.

4. E.J. Mills, Phil. Mag., 1870, 40, 259.

A corollary to the idea of motion was continuity, a phenomenon which Mills defended with equal zeal to his total rejection of any form of discreteness, as exemplified by atoms. Not surprisingly, Mills concluded that the atomic theory conflicted with the homogeneity of chemical substances, an idea which he found unacceptable. 'Chemistry', he asserted,

still looks with half-averted eyes upon all dynamical doctrines. But her great centres of historic conflict are intelligible only by their aid.....chemical substance is homogeneous, not discontinuous substance; chemical functions are modes of motion.¹

To Mills, the success of the laws relating mass of substances to the speed of reaction, discovered by Guldberg and Waage, lay in the fact that it appeared to substantiate his anti-atomistic stand; furthermore, the laws themselves were direct corroborations of his views on the first principles of chemistry - the idea of chemical reactions as a process of continuity, independent of any atomic property. For nowhere is there any sudden increase; if, in a reaction, the partition of the bases and acids in the mixture really take place at first in atomic proportions, it is evident that, being at liberty to act and react, the salts will arrange themselves according to their respective mass, without any reference to their atomic weights.² Harcourt and Esson's work on mass action, which will be discussed in later sections, also

1. E.J. Mills, Phil. Mag., 1870, 40, 259.

2. E.J. Mills, Phil. Mag., 1876, (5th Series), 1, 1.

appears to have provided Mills with proof,

whether the solution contains in each cubic centimetre 746 millionths of a gramme of hydric sulphate, or 150 times that quantity, 604 millionths of a gramme of potassic iodide or 9 times that quantity, or whether hydric chloride or hydro-sodic carbonate be substituted for hydric sulphate, whether the temperature be 0 degree or 50 degrees C. and whether the portion of the change require for its accomplishment intervals of one or two minutes, or intervals of half an hour, this reaction still conforms to the law that the amount of change is at each moment proportional to the total amount of changing substance.¹

that his philosophy on the continuity of matter was valid. Harcourt and Esson's experimental results were analysed by Esson to conform to a smooth hyperbolic function, or rather, in Mills' terminology, as continuous lines. By a similar analogy, Bunsen's famous experiments on the explosion of gas mixtures could also be thought of as a continuous function, each abrupt change being but one of a long unbroken series.² Mills deduced this by a simile, 'we might as reasonably infer, from the striking of a clock at regular intervals, that it had not been previously going, though, in fact, the entire phenomenon is ultimately based on the gradual uncoiling of a spring.'

1. Phil. Mag., 1876, op.cit.

2. ibid.

The principle of continuity was in fact becoming fashionable at that time, and was championed by Ostwald, for instance, in his revolt against atomism.¹ The plausibility of Mills' attempts to bring Harcourt/Esson's and Guldberg/Waage's results to bear on philosophy are lost in his somewhat verbose arguments. In his eulogies on the ideas of motion and continuity, however, Mills was treading a path hardly touched by previous travellers, and barely trespassed upon since, the path between chemistry and philosophy. It is perhaps regrettable that in his determination to proselytize on atomism, he seemingly missed a true analogy between mass, energy and directed motion, each of which he touched upon in turn:

the process of exhausting the chemical energy of a substance, as represented mathematically in logarithmic equations, requires an indefinitely great period of time for its accomplishment. Hence we can understand how chemical action is possible. It can begin because it never has ended.....it appears then, that chemical action is a process at once definite and continuous,as has been stated, matter is directed motion.²

Mills' dynamic ideas in chemistry were described in his

1. See G. Fleck, "Atomism in late Nineteenth Century Physical Chemistry", J. Hist. Ideas, 1963, 24, 110.

2. Phil. Mag., 1876, op.cit.

series of papers often employing expressions, which, today, make strange reading. His excursions, for instance, into the literary - ascribing to the 'perfect majesty of motion', all beauty, all life, and all thoughtful power.¹ It was, perhaps, to the detriment of his fundamental chemical beliefs that he tried, by somewhat histrionic descriptions, to persuade the chemical community to take a more dynamical view of their subject,

.....all remote inspirations, all scattered fragments of knowledge, are but dew or clouds
.....hence forth, for us who have chosen the criterion, all that is good and desirable is motion, all that is evil and to be dreaded is a limit. Let no-one strive to reconcile them.¹

These words did not fall entirely on deaf ears, for it was certainly referred to during the atomic debate.² Mills made frequent references to Williamson's work in his writings, and must have been familiar with the latter's views on chemical dynamics and equilibria. Yet strangely, nowhere in his essays does Mills see the harmony which underlay both his own ideas and those of Williamson's. What distinguished Mills' views from many of those of his contemporaries was his attempt to describe generalizations for the aims of chemistry, in the wider context of universal scientific knowledge. 'The history of the different sciences',

1. Phil. Mag., 1873, (4th Series), 46, 398, 405.

2. Chem. News, 1872, 25, 67.

Mills wrote, 'may be compared to a group of converging series having a common limit - that limit being the law, forever to be desired, from which all phenomena may be deduced....if this be admitted, a criterion of scientific progress becomes possible'.¹ Mills refused to distinguish between his views on the philosophy of science and the fundamental issues of chemical phenomena then being debated. His final ideas on the state^{of}/chemistry were, however, over-pessimistic. Atomism apart, theories of dynamical chemistry were gradually taking shape in that very century. The Kinetic Theory of Gases had laid just such foundations and was not in dispute among the physicists. In the second half of the 19th century, theories of matter and motion were in a much safer state, and far from the evil picture which Mills had painted them to be.

1. Phil. Mag., 1869, 4th S., 37, 461.

2.3 Chemical Affinity and Reaction Velocity: The work of Guldberg and Waage

The work of Peter Waage and Cato Maximilian Guldberg which led to the first mathematical statement of the law of Mass Action in 1864, was aimed, in the chemical tradition of the day, at a better understanding of the age-old problem of chemical affinity.

Peter Waage was born at Flakkefjord, Norway, in 1833. In 1854, he entered the University of Christiania to study medicine. Even as a medical student, his interests were turning more and more to chemistry and mineralogy. Soon after passing the first of his medical examinations, he abandoned the study of medicine for science.¹ His chemical background was thus similar to many of the earlier chemists, whose interest in the subject frequently stemmed from their training in medicine and 'Physick'.

In his fourth year at the University, Waage won an award which enabled him to study in the laboratories of Robert Bunsen in Heidelberg. Bunsen had made several investigations into affinity at the beginning of the 1850s,

1. Obituary Notices, J. Chem. Soc., 1931, 77, 591-593.

and quite probably it was there, under the influence of Bunsen, that ideas which inspired Guldberg and Waage's later work in seeking a quantitative expression for chemical affinity began.¹ On returning to Oslo, Waage became Professor of Chemistry at Christiania in 1862. There, Waage began a life-long friendship with Cato Guldberg, a mathematician, who later became his brother-in-law. Regularly, on Saturday afternoons, they met with other members of the University "to discuss physical and chemical problems".²

As yet the subject of Physical chemistry was fresh territory, but it was an area of interest which the two men shared. Apart from his chemical interests, which led him to investigate chemical equilibria, Guldberg also did considerable work on the forces and laws determining movements of the

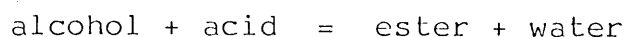
1. R. Bunsen; Ann. Chem. Pharm., 1853, 85, 137.

2. The Law of Mass Action: A Centenary Volume 1864-1964,
Pub. by Det Norske Videnskaps - Akademi i Oslo, 1964, 37.

atmosphere.¹

Waage, in the meantime, concentrated on many problems relating to both chemistry and physics, investigating such problems as the melting of alloys, mixtures of fatty acids and salts. During the early years, Waage also devoted a considerable part of his time in the derivation of an equation of state for gases, liquids, and solids, from a molecular, kinetic approach.² Against this wide background, the two men began experimental investigation of chemical affinity, around 1861.

The work of Berthelot and Pean de Saint-Gilles on esterification served as an introduction to Guldberg and Waage for their study of chemical equilibria.³ In their investigations of the system



Berthelot and Saint-Gilles had established that the reaction does not reach completion but progressively approaches a limit corresponding to equilibrium.⁴ They discovered that equilibrium was attained whether equivalent amounts of acid and alcohol or of ester and water were the starting point.

1. C.M. Guldberg et H.Mohn, Études sue les mouvements de l'atmosphere, Christiania, 1876.

2. Centenary Volume, op. cit., 37.

3. Forhandlinger i Videnskubs-selskaket i Christiania, 1864; J. Prakt. Chem., 1879,(2),19:69-114; see also E.W. Lund J. Chem. Ed. 1965, 42, 548.

4. M. Berthelot, L. Péan de Saint-Gilles, Ann. Chem. Phy. 1862,(3),65,385; 1862,66,5; 1863,68,225.

The amount of product formed at any instant, they found, was proportional to the product of the reacting substances and inversely proportional to the volume. By experimenting with several combinations of acids and alcohols, they finally established that the equilibrium position was almost always the same in each conversion and varied only between 61 to 72 percent, using equivalent amounts. These investigations, which extended over only three years, came to an end in 1863 with the death of Saint-Gilles, at the early age of thirty-one.

Before turning to the study of organic systems in their work, Berthelot and Saint-Gilles had pointed out that the usual systems of acids, bases and salts were not suitable for equilibria studies because the speed of the reactions discouraged the use of any analytical method known at the time; any disturbance of the system resulted in the destruction of the equilibrium. By choosing an organic acid and alcohol, they obtained a homogeneous system whose relatively slow rate of change permitted analysis at reasonable intervals of time, both before and after the equilibrium state had been attained. The reaction times they investigated ranged from several minutes to months; at different time intervals small portions of the acid-alcohol mixture was removed from the reaction vessel and the amount of acid present in the sample found by titration with barium hydroxide. The point of equilibrium was taken to be achieved when successive portions of the samples remained constant in proportions of reactants and products. So close to establishing the influence of mass action on reaction velocity, Berthelot and Saint-Gilles nevertheless failed to take into account, in their

velocity equation, the effect of the reverse action, though clearly recognising the importance of their discovery.

Guldberg and Waage were certainly aware of these discoveries of Berthelot and Saint-Gilles, when beginning their investigations, to which they refer in their first paper, published in 1864.¹ But for some reason, they began their investigations on a totally different, heterogeneous, system, the reaction between solid barium sulphate and a solution of potassium carbonate, together with the reverse reaction between solid barium carbonate and potassium sulphate solution.

The choice of a heterogeneous system for study by Guldberg and Waage may have been influenced by an earlier work on the concept of chemical equilibria, by R. Phillips.² Fifty years earlier, Phillips investigated the reversible reaction of barium sulphate and potassium carbonate and discovered that the final mixture contained all four products, whether he began with these salts or conversely with barium carbonate and potassium sulphate.

The results of their initial investigations were published in Norwegian, and presented to the Christiania Academy of Science and Letters; it introduced their classification of chemical reactions into simple and composite and stated that a composite reaction can be considered as consisting of a sequence of several simple reactions.³ The idea

1. Forhandlinger i Videnskabs-Selskabet i Christiania, 1864 (1865), 35-45; abridged translation by Abegg, Ostwald's Klassiker, 1899, 14, 3-9.

2. R. Phillips, J. Sci. Arts., 1817, 1, 81-86.

3. Centenary Vol., op.cit., 39.

that chemical reactions may occur in several stages was as yet not established, though not entirely new. Guldberg and Waage's concept of chemical sequence appears to have been a great foresight into reaction mechanisms which were not to emerge for some time; but in their own experimental work, they tended to deal only with simple reactions of which their 'composite' reactions were composed.

The reasoning which led eventually to the equilibrium equation was based on the laws of classical mechanics, with which Guldberg, as an applied mathematician, would have been most familiar: assuming that strong chemical forces are acting during a reaction of the simple type $A + B = C + D$, there is a limiting state when all four substances are present simultaneously. Under such conditions two opposing forces must be working at the same time and by careful selection of experimental conditions, a state of equilibrium can be achieved, similar to that reported by Berthelot and Saint-Gilles. At equilibrium, the two opposing forces balance, as in a mechanical system; the equation representing chemical forces was thus developed by analogy with Newtonian Law, so that chemical equilibrium was attained when action and reaction were equal and opposite. From their paper of 1864:

In order to study the chemical force we have chosen the conditions where the formation and decomposition are taking place at the same time. In this case, the forces which produce the formation of the two molecules and those which decompose these molecules in regenerating

the original molecules, are acting at the same time and give rise to a state of equilibrium.¹

The system they chose, $A + B = A' + B'$ was a double decomposition reaction, to which they assigned specific coefficients:

When two molecules A and B with masses M and N tend to form the two new molecules A' and B' by a substitution of their elements, the total volume being V, the force which tends to produce this substitution may be expressed by

$$\propto (M/V)^a (N/V)^b$$

where a and b are specific coefficients for the species.....Let us suppose that one has a system of four substances A, B, A', B' with masses p, q, p', q' respectively. When the state of equilibrium is attained, the quantity x of A and of B is transformed into A' and B' and the masses are p-x, q-x, p'+x and q'+x. The force which tends to form A' + B' will be

$$\propto [(p-x)/v]^a [(q-x)/v]^b \quad (i)$$

and that which tends to form A + B will be

$$\propto [p'+x/v]^{a'} [(q+x)/v]^{b'} \quad (ii)$$

These two forces are equal and one obtains the equation

$$(i) = (ii) \quad 2$$

-
1. Les Mondes, 1864, 12, 107; J. Chem. Ed., 1965, 42, (10), 548.
 2. E.W. Lund, J. Chem. Ed., 1965, 42, (10), 548.

The formulation of this equation by Guldberg and Waage quantified for the first time the actual amount of substance taking part in chemical reactions at equilibria. The term 'active mass' appears to stem from Berthelot and Saint-Gilles' earlier work on esterification, in which they stated that only a part of the alcohol and acid present in the reaction was 'active'. Their velocity equation actually gave the reaction rate as proportional to these 'active' masses, saying:

le quantité d'éther produite à chaque instant
est proportionnelle au produit des masses actives
qui sont en présence.¹

Somewhat puzzlingly, although the two French workers stated the dependence of velocity on active mass, and clearly realised the occurrence of conditions at equilibrium, they failed to account for it in their rate equation. The term 'active mass' as used by Guldberg and Waage was not the same as that conveyed by the two French authors; though still somewhat confusingly referred to as the 'law of mass action', Guldberg and Waage's terminology referred merely to concentration. In their paper, published in Norwegian, two forms of the law were given, one relating to mass action and the other to volume action; later by using the concept of concentration, the two laws were united to that of 'active mass'. In their later paper of 1879, the two authors defined their concept of active mass as follows:

1. M. Berthelot, L.P. St-Gilles; Ann.Chem.Phys., 1862, (3), 65, 385.

The mass with which a definite substance enters the unit volume of the body in which the chemical process proceeds we have called the active mass of the substance. Actually, we mean by the active mass only the mass of the substance within the sphere of action; under otherwise equal conditions, however, the action sphere can be represented by the unit volume.¹

In order to derive a rate equation, Guldberg and Waage turned their attention to the influence of time on chemical reactions in the summer of 1864. Using the same notation as before:

Let us assume that the new bodies A' and B' do not react. Let p and q be the number of molecules of A and B, v the velocity, t the time, and x the quantity which has transformed during this time. Then one has, regarding the total volume to be constant:

$$v = dx/dt = k(p-x)^a (q-x)^b$$

where k is a constant depending on the nature of the bodies, the volume, the temperature and the solvent.²

The vital step which had been neglected by Berthelot and Saint-Gilles, that of the reverse reaction, was taken into account by a similar deduction, that the rate of reaction

1. J. Prakt. Chem., 1879, (2), 19, 69.

2. E. Lund, J. Chem. Ed., 1965, 42, 10, 548.

at any instant is proportional to the driving force, derived in their first paper.

Then, let us consider the more general case where the new substances A' and B' react and give the original bodies A and B. The force which tends to produce A + B is equal to $\propto ax^{a'}x^{b'}$ and, putting $a'+b' = n$, one has the velocity

$$v = dx/dt = k[(p-x)]^a [(q-x)]^b - \alpha x^n$$

In this case a state of equilibrium is attained for a certain value of x.¹

Under equilibrium conditions, the velocity v is zero. Though Guldberg and Waage had correctly formulated the conditions for chemical equilibria, they did not appear to realise that the powers to which the concentrations had to be raised were dependent merely upon the integers deducible from the chemical equation.² More importantly, they did not distinguish between the general rates of reaction depending on 'active mass' (i.e. mass of substance within the sphere of action) and the derivation of their equation based on equilibrium conditions. This early failure to fully comprehend the significance of dynamic equilibrium was to lead to many misunderstandings and confusion in the years to come. Guggenheim, for instance, maintained that errors in contemporary chemical text books can be traced to misconceptions arising from Guldberg and Waage's original 'Law of Mass Action'.³

1. E.Lund, J.Chem. Ed., 1965, 42, (10), 548.

2. Centenary Vol., p. 40.

3. E.A. Guggenheim, J. Chem. Ed., 1956, 33, 544-545.

By this time, the concept of dynamic equilibrium had been in existence for some fifteen years, in so far as Willllamson's paper of 1850 was concerned. But it is doubtful whether the complexity of chemical equilibria was truly understood. For both Guldberg and Waage and their contemporaries in England, Harcourt and Esson, great difficulties lay in the actual choice of chemical system best to be studied. In retrospect, it is all too easy to forget that in the decade during which the ground for chemical dynamics was being laid, chemists had not the elegant tools of thermodynamics which were still being forged; ionisation of salts in solution was not understood, nor was correct chemical formulation yet established. As already seen, it was a time when even the basic concept of atoms was still being hotly debated, in England at least.

Three years after their first publication, Guldberg and Waage published a more elaborate analysis of their findings, this time in French.¹ Beginning with the ideas of Bergman and Berthollet on affinity, they pointed out that there are distinctions between mechanical and chemical forces of attraction.² In a chemical system, forces are acting between all pairs of molecules present and at very short distances. They suggested that reactions occurred within a 'sphere of attraction', outside which chemical forces were inactive. The strongest forces of 'affinity forces' were those acting between the substances A and B, but they introduced the theory that

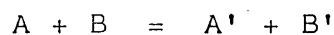
1. C.M. Guldberg, and P.Waage; Études sur les Affinités Chimiques, Christiania, 1867; Ostwald Klassiker, 104.

2. Centenary Vol., p.41.

secondary, weaker forces were also acting between all other pairs of molecules present in the reaction. The picture of their system was that:

Within the sphere of action there may be, besides the reactants A and B, several other species X, Y, Z, which are called 'foreign substances'. Between all these substances there are forces acting.¹

These latter forces may retard or accelerate the reaction, an interesting idea which unfortunately was too complicated for them to develop satisfactorily. In order to simplify their analysis Guldberg and Waage resorted to ideal reactions in which secondary forces were neglected. Here they introduced 'active mass' to represent the mass of substance contained within 1cc. of the total volume, and for the first time combined their earlier laws of mass and volume action to that of concentration or law of active mass. As before, the reaction was



for which they gave the general equilibrium equation where p, q and p', q' are the active masses of A, B and A', B' respectively and k, k' are affinity coefficients, following a notation first used by Bunsen in 1853. They did, however, attempt to account for the observed qualitative difference between the influences of A and B by introducing two further coefficients, m and n, such that the proper equilibrium equation took on the complicated form:

$$k p^m q^n = k' p'^{m'} q'^{n'}$$

1. Centenary Vol., p.41.

In their studies, Guldberg and Waage carried out some three hundred experiments covering a very comprehensive list of different classes of reactions including:

- systems of four soluble substances
- systems of two soluble and two insoluble substances
- systems of three soluble and one insoluble substance
- systems of arbitrary number of soluble substances
- systems of soluble substances and gaseous substances which are absorbed by the solution
- systems composed of gaseous substances produced by the dissolution of a solid substance and also
- systems of gaseous substances.

In addition, the two authors tested their theories on the experimental results of earlier workers including Berthelot and Saint-Gilles, Brodie's experimental values for reaction between barium peroxide and hydrochloric acid and the earlier results of Debus and Scheerer.¹

The agreement between experimental and predicted results was deemed satisfactory. But it was not until the Danish thermochemist Julius Thomsen applied their equilibrium

1. See: C.M. Guldberg, P.Waage, Avhandl-Norske Videnskaps-Academi Oslo, Mat. Naturv. Kl. 1864, 35; an account of this is given by E.W. Lund, J Chem.Ed., 1965, 42, 548-550; see also M.M. Pattison Muir, A History of Chemical Theories and Laws, London, 1907. Reprinted: Arno Press, New York, 1975, 404; B.C. Brodie, Ann.Phys.Chem., 1863, 120, 294; J.R. Partington, A History of Chemistry, London, 1964, Vol. 4, 588-595.

equation in a paper of 1869,¹ followed by the publications of Horstmann in 1873 and 1877² that Guldberg and Waage's work became generally known. This encouraged the two Norwegians to re-publish their earlier ideas and results in 1879.³

But the essence of their work had been summarised very well towards the end of their paper of 1867:

These are the series of experiments to which we have applied calculations. We think they are sufficient to establish the probability of our theory; the divergences between the observed and the calculated results are due to something which we have neglected, the presence of salts formed during the reactions, and, in many cases, certain coefficients of action which are probably not sufficiently small to be neglected....beginning our studies in 1861, we thought it might be possible to find numerical values for the magnitudes of chemical forces. We also thought that we might find for each element and for each chemical compound certain numbers which would express their relative affinities, as atomic weights express their relative weights.....⁴

1. J. Thomsen, Ann.Phys.Chem., 1869, 138, 65.

2. A. Horstmann, Ann.Chem. and Pharm., 1873, 170, 192; Ostwald's Klassiker, 137; Verhand.Naturhist.Med.Ver.Heidelberg, 1877, 1(5), 465;

3. J.Prakt.Chem., 1879, 2, 19, 69; Ostwald's Klassiker, 104

4. C.M. Guldberg, P.Waage, Etudes sur les Affinités Chimique Christiania, 1867; Ostwald Klassiker 104.

It would appear that, even in 1867, ideas of chemical affinity were proving more elusive than might have been anticipated and that, had it been possible, Guldberg and Waage would have removed the concepts altogether from their work, as indeed Harcourt and Esson were to do. However, at the end of their work, they were unable to resolve these perplexing problems and their account in fact describes accurately the state of progress at the conclusion of their labours:

....although we have not solved the problem of chemical affinities, we think that we have indicated a general theory of some chemical reactions, namely, those wherein a state of equilibrium is produced between opposing forces....The aim of our memoir has been to demonstrate, first, that our theory explains chemical phenomena in general, and secondly that the formulae which are based on the theory accord sufficiently well with the numerical results of experiments....All our wishes would be accomplished if we could succeed in drawing the serious attention of chemists, by means of this work, to a branch of chemistry which has undoubtedly been too much neglected since the beginning of this century.¹

Between the years of 1867, when Guldberg and Waage had completed what was to be their major contribution to chemical

1. C.M. Guldberg, P. Waage, op.cit., 1867.

dynamics, and the end of the century, the branch of chemistry in which they were undoubtedly among the pioneers was to be firmly established. It was rapidly becoming a period of change in the study of chemical processes; not only equilibria, but dynamic equilibria, not only atoms but atoms in motion. The kinetic theory and the concept of energy conservation were growing ideas whose presence were impinging themselves on the consciousness of the chemists of the day.

2.4 Time and Chemical Change: The Work of Augustus Vernon Harcourt and William Esson

2.4.1 Introduction

Historically, the inherent^{ly}/complex nature of chemical change had always been realized. Qualitatively, at least, the role of time in chemical phenomena had long been appreciated - iron took time to rust, blood to coagulate and colours to fade. The very complexities of these reactions no doubt contributed directly to the aura of mysticism which marked the work of the early alchemists. But by the middle of the nineteenth century, it may be surmised that chemists had recognized that the formation of a chemical compound is only the concluding act of a complex series of changes; changes which begin the moment the reacting substances are brought into contact, and which take place continuously until the products appear in their final state. In 1852, Schönbein^{en} had said with considerable foresight:

And it appears to me that those states which exist before the so-called chemical combination has taken place constitute the most important part of chemistry, the peculiar dynamics of our science.¹

1. C.F. Schönbein, J. Prakt. Chem., 1852, 2, 55, 1.

By 1898, chemists had discovered that it was the slower stage of these multi-step reactions which determines the actually observed speed of reaction. As Walker put it:

The time occupied in the transmission of a telegraphic message depends both on the rate of transmission along the conducting wire, and on the rate of progress of the messenger who delivers the telegram; but it is obviously this last, slower rate that is of really practical importance in determining the time of transmission.¹

The elucidation of the various stages by which the final products are obtained thus represents a very real and vital stage in the evolution of chemical science. The work of Augustus Vernon Harcourt and William Esson represents the first attempts to resolve the stages within a chemical change and the rates at which these occurred. Their work spans the vital fifty years between the first quantitative work of Wilhelmy and the establishment of rate studies as a distinct chemical discipline now designated as physical chemistry. The importance of the determination of rates of change in chemical processes was the light that this could throw on problems which, up until then, were highly obscure - the ways and means by which chemical changes are brought about.

1. J Walker, Proc. Roy. Soc. Edin., 1898, 22, 22

The subject of reaction mechanism was only made possible by first understanding the characteristics of chemical change.

2.4.2. Rates of Reaction and the Concept of Chemical Change

The weekly Friday evening meeting at the Royal Institution on February 28th, 1868 was devoted to a paper delivered by Vernon Harcourt, entitled "On the Rates at which Chemical Actions take place". This summarised the results of work which Harcourt had achieved in the four of five proceeding years but also, amazingly, contained ideas germane to his chemical thinking for the halfcentury yet to come.

Chemistry may be defined as the science which investigates the relations of the different kinds of matter one to another,

wrote Harcourt,

and whose changes, under changed conditions or by contact one with another, form the subject of study.¹

The point Harcourt raised on that occasion was that the study of chemical change involved two factors, not merely the result of the chemical reaction but also the course of the chemical change. As an example of this dual nature of chemical change, Harcourt compares the chemical changes wrought by fire on coal, reminiscent of Faraday's famous lecture on the history of the candle. The points made by Harcourt were vital ones, for they amounted to a criticism of chemistry as it was then practised

1. Proc. Roy. Inst., 1868, Vol. 5, 304-8.

in Britain. The problems which he considered the chemist had yet to resolve concerned the careful study of actual processes: those relating to the rates at which chemical changes occurred, and under what conditions; were the changes simple or multiple? and were the changes independent, successive or simultaneous?¹

PLEASE TURN TO P. 162

1. These are Harcourt's terminology. Interestingly, J.W. Mellor in his Chemical Statics and Dynamics, first published in 1904, introduces his book in precisely the same way, on page 1:

The relative influence of one form of matter upon another has attracted the attention of observers from the earliest ages. Matter appears to be endowed with properties by virtue of which two or more dissimilar substances, when brought into close contact, give rise to other forms of matter possessing properties quite distinct from the original substances. The process of change is called a chemical reaction. Chemical reactions may be studied from different points of view. For example, we may confine our attention to:-

Footnote continued from P129

- I. The result of the change, and ask, what kinds of matter have ceased to exist? What kinds of matter have come into existence?.....
- II. The course of the change:- Is it simple or does it consist of several changes? Are these dependent or independent, successive or simultaneous? At what rate does the change occur?
- III. The Circumstances modifying the change. Under what conditions does the reaction occur?.....

And this is the purpose of chemical science, to describe in the simplest possible manner the phenomena associated with matter in the act of changing.

The connection between Harcourt and Mellor is a very direct one; Mellor dedicated his book to H.B. Dixon, one of Harcourt's first pupils. Mellor's book was the first textbook on chemical kinetics of its kind and summarised the state of the subject some fifty years after the first rate measurements by Wilhelmy. It was to influence several generations of physical chemists. For example, in his obituary of Nevil Sidgwick, H. Tizard recalls his first meeting with his tutor in 1905:

He turned to his shelves and picked out a new-looking book entitled Chemical Statics and Dynamics by Mellor. "This is an important subject", he said, but the book is rather too mathematical for me".

Footnote continued

Sidgwick was, in Tizard's words, - "fortunate in his tutor Vernon Harcourt, the Dr Lee's Reader in Chemistry, who was a pioneer in the new domain of physical chemistry, and one of the first to measure the velocity of chemical reactions and to study the conditions that determined it". Sidgwick was greatly influenced by Harcourt, and did the whole of his practical work in the Christ Church Laboratory, under Harcourt's guidance.

Mellor himself had a remarkably productive career. Born in Huddersfield in 1869, he was taken to New Zealand at the age of ten. Later, he attended the University of Manchester, where he worked under Dixon. He later wrote that the writing of Chemical Statics and Dynamics had "given him very great pleasure". Among his many other publications are the 16 Vol. Comprehensive Treatise on Theoretical and Inorganic Chemistry; Higher Mathematics for Students of Chemistry; and A Treatise on Quantitative Inorganic Analysis in 1912. See: A.T. Green, Nature, 1938, cxlii, 281; J. Chem. Soc., 1943, 341.

In retrospect, the history of chemical development shows how unequally the two aspects of chemical reactions - the products of the chemical change and the course by which they are attained - had been pursued up until that time. As Harcourt pointed out, the study of the results of chemical action had engrossed the attention of chemists almost to the exclusion of the study of their course.¹ The views expressed in this publication were to be the beginning of many similar exhortations by Harcourt to chemists to pay closer attention to the ways and methods by which chemical changes occurred; for only thus could the laws of chemistry eventually be understood and formulated. Speaking almost a decade later as President of the British Association, in 1875, he continued to maintain that:-

if any chemist not content with a process giving a good yield of some product, examines minutely the nature of the reaction, observing its' course as well as its' final result, he will find much more for study than the chemical equation represents. He will probably also find that the reaction and its conditions are of a formidable complexity and will be driven back towards the beginnings of chemistry for cases sufficiently simple for profitable study.²

1. Proc. Roy. Inst., 1868, (5), 305.

2. B.A. Rep. 1875, (Chem Sec.), 32-36.

Harcourt, not infrequently, contrasted the result of generations of chemists' appetite for ever-new material compounds with the attitude of physicists towards understanding the forces of nature at their disposal.¹ The different number of forces known, such as gravity, electricity, magnetism, heat and light, were relatively small in number. But supposing, he said, that these forces consisted of a large number and were capable of being converted not only into each other, but also into an infinite number of other different forms of distinct forces - would experimental physicists have spent their time transmuting one form into another, neglecting the study of the laws governing their existence? Harcourt believed that physics had advanced because experimentalists had taken care, before all else, to comprehend the conditions under which the known existing forces were produced, by first formulating their laws of behaviour. This constant analogy between chemical development and that of physics was characteristic of Harcourt, who was himself amongst the first generation of trained "professional" chemists in Britain. He was to retain this physical focus throughout his long years of chemical endeavour. In 1881, writing to his former pupil, Sir John Conroy, he admitted:-

I generally find physics, when within my
comprehension, more interesting than chemistry....

1. Proc. Roy. Inst., 1868, (5), 305

and the morning I most enjoyed was the last which I spent listening to Sir William Thompson on meteorites, incandescent vacuum lamps and photometry.¹

Nevertheless, this analogy between physical and chemical systems could not sensibly be taken too far. Indeed, Harcourt pointed out, there were reasons as to why chemists had neglected the study of the course of chemical change. Such studies were beset with difficulties - both experimental and theoretical in nature. For, despite the vast number of chemical reactions known, few existed which were capable of close observation over the entire course of change. The time factor was a vital one in understanding how chemical changes occurred but the velocity with which the majority of reactions occurred prohibited close scrutiny. This was particularly true for simple type reactions which would have facilitated investigation. The problem for chemists, as Harcourt saw it, was either to find means by which very great reaction velocities could be estimated - as had been done in physics by the measurement of the speed of light - or it was essential to search for a chemical change whose speed permitted experimental observation.²

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1. The Conroy Papers, Balliol College Library, Oxford
 2. For chemists, the means by which very small time intervals could be measured did not occur until the present century with the introduction of flash photolysis. See G. Porter: Flash Photolysis and some of its Applications, Nobel Lecture, 1967.

Throughout his years of chemical teaching at Oxford, Harcourt was to take his own admonishments with true zeal - searching endlessly for a suitable chemical system to demonstrate the hidden complexities within the process of chemical change. In 1896, as President of the Chemical Society, he lamented the loss to chemistry due to a lack of understanding of the nature of chemical change at a deeper, more significant level. Recalling the original aims of the Chemical Society, to gradually furnish a Museum of Chemistry from a collection of chemical specimens, which were, however, dispersed when the Society moved its location from the ground floor of the original Burlington House, he wrote:-

Many other specimens had succumbed to the property of slow chemical change, a property existing, no doubt, in a number of substances which, in our hurried way, we deal with before the year is out, and we are not content to watch. It might by now have been of great interest to examine some of the decomposed specimens of this miscellaneous collection.¹

In his retiring address as President of the Chemical Society, entitled A Few Thoughts on the Question whether the Changes which Matter undergoes are different in their Nature, the idea of change still strongly persisted.² Harcourt argued that there was no fundamental distinction between

1. J. Chem. Soc. 1896, LXIX, 563

2. J. Chem. Soc. 1897, LXXI, 595-597

the changes taking place when a compound such as potassium chlorate (KClO_3) was heated, giving potassium chloride and oxygen, and the changes occurring when, say, phosphorous pentachloride was similarly heated, giving phosphorous trichloride and chlorine. But, he said, chemists insisted on distinguishing these changes by calling the first change a decomposition and the second a dissociation; the distinction being that, whereas in the first case the products did not recombine on cooling, the second did.¹ The nature of the chemical change in the two cases, as Harcourt saw it, did not differ - all consisted of changes of molecules of one kind into molecules of another kind; the two kinds differ only in the nature, number and arrangements of the atoms making up the molecule. A journey is the same journey, he declared, whether it is made with a return ticket, or whether the person returns by a different route.²

Harcourt's arguments were not ones of terminology nor classification but, more fundamentally, that chemists should look closer at the nature of chemical change and:

not slur over such a fact as the formation of definite compounds with water, nor place this change and these compounds in a separate class because they seem to lie outside a system of

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1. The term dissociation had been coined by Henri-Sainte Claire-Deville in the years 1857-1866. During these years, he investigated a large number of reactions which decomposed spontaneously at high temperatures, reforming when the products were allowed to cool in contact; Compt. Rend. 1857, 45, 857-861
 2. J. Chem. Soc. 1897, LXXI, 595-597

representation which embodies some great generalisations - a change is not less a change, nor is it another kind of change, according to the degree of facility or directness with which it can be reversed.¹

On a previous occasion, Harcourt had raised a similar problem, that because of the rapid advances in science, chemists were in danger of mistaking verbal for real questions.² For chemists, the problem remained not only one of structure and chemical change but also, even more fundamentally, that of chemical notation. The particular question in hand was the definition of an acid.³ Complications occurred constantly because different chemists were applying to different substances the familiar names of sulphuric, nitric and carbonic acids. At the time Harcourt was talking, 1867, these names still frequently referred to the various oxides of sulphur, nitrogen and carbon respectively. But since these compounds were known to exhibit their acidic properties only in the presence of water and at the same time there existed acids which, while possessing hydrogen, lacked oxygen, a new system had come into common use - the word acid was associated with the hydrated form of the oxides and the term anhydride applied to the replaced oxide. The question of which term was the correct usage remained a controversy - but, as Gerhardt said, all

1. J. Chem Soc., 1897, LXXI, 596, 597

2. Chem. News, 1867, 16, 272

3. The same question remains one of complexity today, with the Arrhenius, Bronsted-Lowry, and Lewis Theories all in use; see for example, H.J. Emeleus, A.G. Sharpe, Modern Aspects of Inorganic Chemistry, 1973, 139

discussion remained somewhat sterile when the disputants were agreed as to facts and differed only about the meaning of words.¹ Harcourt advocated that the substance whose symbol was CO_2 should be "carbon dioxide", and anhydrous sulphuric acid, (SO_3) be "sulphur trioxide"; the salts of these acids would be, for example, sodium carbonate, nickel sulphate. Harcourt's influence as a teacher of chemistry may have been considerably greater than has been recognised, as the modern acceptance of these terminologies infers. Also recognised today, and advocated by Harcourt in 1867, were the two forms of iron sulphates, "ferrous sulphate" and "ferric sulphate".²

Harcourt's ideas on the importance of the course of chemical change and the role of time in chemical reactions emerged very early in his work and remained ones of priority throughout his chemical career.³

Harcourt also persistently distinguished between the study of the nature of a chemical change from the practical exercise of carrying out chemical experiments. To look cursorily at the apparent sudden appearance of rate studies in the published work of Harcourt, to be joined only later by Esson, gives a curiously static picture, far removed from the dynamic field of chemical kinetics of which their work

1. Chem. News, 1867, 16, 272

2. ibid.

3. Harcourt was not a prolific writer. With rare exceptions, nearly all his published work deals directly with chemical rates of change.

formed a pioneering nucleus. It is not difficult to understand why generations of chemistry students and textbooks have referred to the "classical work of Harcourt and Esson". Certainly the summation of their combined efforts is unusual, if not chemically unique, following as it did, a path laid over a period lasting almost half a century, in which much progress was made but from which little deviation took place. It is another interesting factor in this apparently static picture that countless students have repeated the experimental results and techniques of Harcourt and Esson's work without producing superior results; the classical image remains to the present day.

Tracing the origin of Harcourt's ideas on time and rates of chemical change is not easily achieved since few personal writings appear to have survived.¹ To follow Holt's definition² of pre-requisite conditions, in a given time and place, which cause the communication of ideas in a particular discipline to become significantly effective:-

- (i) ideas necessary for the emergence of a new discipline are usually available over a comparatively long period of time and in various places.

1. I wish to thank Mrs Schiele and Pamela Schiele, of Headington, Oxford, daughter and grand-daughter of A.G.V. Harcourt for the information imparted to me at various times throughout this study.

2. B.W.G. Holt, B.J. Soc., 1970, 21, 181-199

- (ii) only some of these embryos continue in further growth.
- (iii) such growth occurs in time and place because individuals become interested in the new idea, not only for its intellectual content but also as a means to the end of a new intellectual identity and, even more importantly, a new occupational role.
- (iv) the conditions under which such interest emerges can be identified and form the basis for building a predictive theory.¹

produces an interesting picture of Harcourt's work, far removed from the static one which the mind first entertains; the conditions set by Holt, (i) - (iv), describe accurately the time, place and conditions which form the background to Harcourt's life and work. Studies relating to the rate at which chemical reactions proceed in isolated cases had been undertaken by contemporary or near-contemporary workers prior to that of Harcourt and would most likely have been known to him. Among the earliest were the investigations of compound esters from the interaction of acids and alcohols by Berthelot and St. Gilles around the beginning of the 1860s. Another influence which clearly had repercussions on the later work of Harcourt and his many subsequent students was the investigations of gas explosions done by Bunsen at Heidelberg. A special case of simultaneous discovery is

1. B.G.W. Holt op. cit.

the work of Harcourt and Esson's contemporaries, the Norwegians Guldberg and Waage to whom are usually attributed the "Law of Mass Action".

Historically, the phenomena of time can be traced faintly among work of the alchemists and those subsequently seeking to dispel the mystical elements of chemical processes, as Van Helmont demonstrated. Intellectually however, the ideas of the course of chemical change and the rate at which this occurred are ones which, undeniably, belong to Harcourt. They form a continuity of thought throughout his chemical writings, as will be seen in the subsequent pages. The establishment of Harcourt's ideas on time factors in chemical processes is also important from another point of view. His own research was the foundation from which later sprang a large number of pioneering studies on the rate of reaction of other systems, including gases and homogeneous and heterogeneous phases, at Oxford. The new "occupational role" which emerged from Harcourt's studies was that of teacher to a new generation of students concentrating on the study of laws governing rate processes. During his long years as a teacher of chemistry at Oxford, Harcourt constantly encouraged those who came under his influence to pursue similar chemical research. To a former pupil, Sir John Conroy, who himself later became a teacher at Oxford, Harcourt wrote:

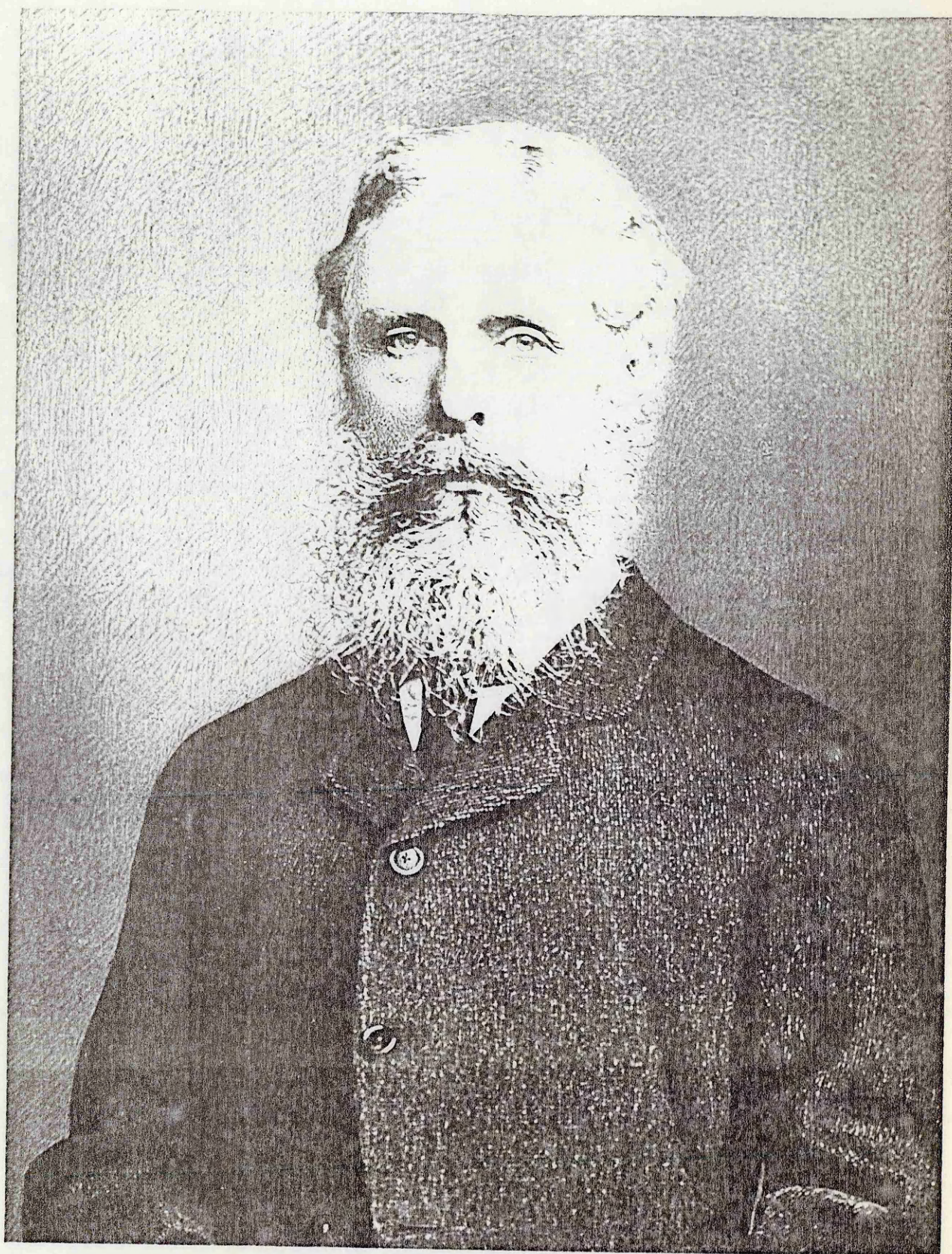
March 1876

... I wish you would undertake some case of gradual chemical change. There is so much

to be done in that line, and it needs neither a number of chemicals nor elaborate physical apparatus. Here is a case I have noted as worth trying, and the principal chemical is an old friend of yours. I have observed that the aqueous solution of sodium dioxide is fairly stable, also the acidified solution is stable. But if the solution is half acidified it decomposes rapidly. Perhaps the change is $\text{Na}_2\text{O}_2 + \text{H}_2\text{O}_2 = 2\text{NaHO} + \text{O}_2$. But it would be very interesting to observe at what rate the decomposition proceeded with different proportions of acid, and very easy since the decomposition can be at once arrested by pouring in an excess of acid and the residue of dioxide determined with permanganate.¹

Before turning to a discussion of Harcourt's work on chemical change, it is interesting to take a closer look at the background which pioneered fifty years of devotion to the study of reaction rates.

1. The Conroy Papers; Balliol College Library, Oxford.



Portrait of Augustus G. Vernon Harcourt (1834-1919)

2.4.3 The Oxford of Augustus Vernon Harcourt (1834-1919)

(a) Early Days and Influences

Harcourt's background was a privileged one. The son of Admiral Vernon Harcourt, and grandson of the Archbishop of York, he was educated on classical lines, first at Cheam, and then Harrow, before entering Oxford in 1854. It appears that Harcourt had originally intended to read Classics but his chemical studies on entering Balliol College seem to have begun without much delay. This auspicious switch from classics to chemistry was to be repeated some years later when Harcourt apparently rescued H.B. Dixon from a similar situation. Dixon was to become one of Harcourt's most famous pupils and his obitunist.¹ The early classical training nevertheless made its mark. Writing to a friend at the end of his life, Harcourt recalled how the first three years of his life at Balliol were given chiefly, but not very industriously, to classics:

One great good I derived from it, was much companionship with Edwin Palmer, Henry Smith and John Conington. I don't mean that my scholarship deserved it, certainly not - Liddell once offered me a classical tutorship at Christ Church but I think I did right to keep to chemistry. There were few chemists then, and plenty of men qualified to take our pass pupils.²

1. Proc.Roy.Soc., 1920, 97, vii.

2. The Times, Monday 25th August, 1919.

Such were the pragmatic reasons for Harcourt turning his interests to chemistry, an interest which was to last more than half a century. Little is known as to the early inspiration for his interest in science, but one who probably exercised considerable influence was his uncle, the Rev. William Vernon Harcourt.¹ William Vernon Harcourt entered Christ Church, Oxford, in 1807 to study for the church. The major influence on his subsequent life-long interest in science in general, and chemistry in particular, can be easily attributed to John Kidd, the early Oxford chemist, who then taught at Christ Church. This interest in science, manifested into action, initiated first the Yorkshire Philosophical Society and in 1831, the British Association for the Advancement of Science. As a nineteenth century churchman, W. Vernon Harcourt's interest and active role in the sciences was not exceptional, but there is ample evidence that his interest was far from that of the occasional 'dabbler'. He corresponded with leading scientists of the day, including Davy, Faraday, Herschel, Airey, Stokes, Babbage and was a close friend of Liebig's.² The majority of his experiments were devoted to the properties of heat and optics, on which he wrote to both Wollaston and Davy. Records show that both Davy and Faraday communicated to him results of significance before publication:

1 W. Vernon Harcourt 1789-1871, fourth son of the Archbishop of York.

2 The Harcourt Papers, 14 vols., Ed: Edward William Harcourt, Oxford, printed privately. See Vol. 13.

From Davy to William Vernon Harcourt

London 21st. January 1824.

I have lately been led to one electro-chemical result which has much pleased me, and which promises to be of great national importance, a simple method of altogether preventing the corrosion of the copper bottoms of ships, and making that imperishable which now only lasts for a few years. It is a deduction from my doctrine that that a feeble chemical action may be destroyed by a feeble electrical action - and the contact of a very small portion of tin sufficient to render a very large surface of copper sufficiently negative to resist the action of sea-water. I am going to try the experiment immediately upon all the ships of war that can be easily brought into port. The result was so conclusive as to be beyond all doubt in all preliminary experiments.¹

1 The Harcourt Papers, op.cit., Vol. 13, 277.

From M. Faraday: R.I. April 16th, 1833
to W. Vernon Harcourt¹

I have been working much lately, but want time sadly. I hope shortly to be able to send you a copy of my paper on the identity of electricities. I finished writing a paper last night which will immediately go into the R.S.² It is principally on a new law of electro-conduction, which law possesses very general influence. Under it, bodies in the solid state which perfectly insulate electricity of a certain tension so soon as they are liquified, become excellent conductors. It is a remarkable thing in these bodies to contrast the conducting process for heat and electricity as the states are changed, the one is suddenly lost, the other as suddenly gained. I mention these things to you knowing your love for science. I have been sufficiently annoyed in former cases to desire in all future ones that no accidental chance or mistake as to right etc. should arise that reasonable precaution will prevent. I would rather not have my mouth thus shut, but I find it safest.³

1 R.I. The Royal Institution.

2 R.S. The Royal Society.

3 The Harcourt Papers, op.cit. Vol. 13, 312.

Elected to the Royal Society in 1824 on the personal recommendation of Davy,¹ W. Vernon Harcourt nevertheless considered the Society's grievous shortcomings as conducive to the founding of a new association for the advancement of science. The incomparably prestigious Royal Society was becoming, as a body, lacking in inspiration and unable to inspire the activities of even its own members. Particularly notable at this time was its financial state; possession of wealth appeared to have played no small role in determining the election of its Fellows.²

In contrast, the Rev. Vernon Harcourt intended the new society for science to be one which would not:

separate writers from readers, the
professor of natural knowledge from
the student.³

Echoes of similar attitudes to education, and that of science in particular, were to appear in the Rev. Vernon Harcourt's nephew many decades later, including a notable degree of foresight and progressive liberalism.⁴

1 See Harcourt Papers, Vol. 13, 196.

2 William Vernon Harcourt: Report of the First and Second Meetings of the British Association for the Advancement of Science; York 1831, Oxford 1832. Reprinted in part in Science before Darwin, ed. I.B. Cohen, H.M. Jones, 1963, 289-304.

3 ibid. p. 289: Interesting to the present study, Vernon Harcourt listed the measurement of time as amongst the finest scientific heights achieved under the Royal Society's auspices.

4 In his address as President of the B.A. in 1875, Harcourt advocated science education in schools, not only for well-to-do young men, but for women too; he insisted that 'neither the reason of the case, nor the jealousy of the dominant sex, nor partial legislation excludes women from sharing this pursuit (of chemical inquiry) with men'.

But in the academic and scientific atmosphere which prevailed in nineteenth century Britain, it was perhaps the more subtle but vital factors affecting social and economic development which were to shape the future of the chemist's role. It is something of an irony that the pervading degree of liberalism epitomised by the Rev. William Vernon Harcourt towards scientific progress was to produce another effect. His sole criterion for admission to the new scientific society, - which was to encourage all personages who possessed the 'zeal for science', may well have eventually disqualified Vernon Harcourt himself from being identified with the new scientific bodies which were shortly to arise. As an established clergyman, he was, undeniably, a member of that élite group which was long accustomed to 'occupying the idealistic role of the amateur scientific savant'.¹ Thus, despite his role in the struggles for the acceptance of science into society, as an established member of the Church, his 'qualifications' would have increasingly divorced him from the new breed of chemists which was to emerge after 1877, only six years after his death. Although he had continued with scientific speculations which could be considered as being original, and with 'a true zest for science', the emergence of chemistry as a 'real science' was to become increasingly

1 B.W.G. Holt, Brit.J.Soc., 1970, 21, 181-199; see also F.M. Turner; 'The Victorian Conflict Between Science and Religion: A Professional Dimension'. Isis, 1978, 69, 356-376.

associated with professionalism. Full-time occupation with chemistry was to be the major criterion for the new professional chemist.¹

During much of the nineteenth century, the role of science and those practising it, as well as its status in education, was the subject of radical reform in Britain. The road by which the establishment of science into the Oxford curriculum was achieved was a long and complicated one.² The movement by a few members of the University to introduce some branches of natural science among the already established subjects to be examined for a degree at Oxford, was accelerated by a visit of the British Association for the Advancement of Science in 1847. Amongst the leading members of this controversial movement was Charles Daubeny, then Professor of Chemistry and Botany, and Richard Acland, the Lee's Reader in Anatomy. Acland, in a published letter, pleaded that:

1 Generally, for those practising and teaching Chemistry in Britain, recognition as an independent occupation in the professional register did not occur until the late 1870s. The formation of societies devoted entirely to the interests of the professional chemist played a major role in establishing the status of chemical pursuits. In keeping with this tradition, Harcourt's sponsor, in his election papers to the Royal Society in 1868, had written 'none' against the query, Profession or Trade. For recent studies in the establishment of chemistry and science in Britain, see: C.A. Russell, G.K. Roberts, N. Coley, Chemists by Profession, Open University Press, 1977; F.M. Turner, op.cit.

2 For a general background to education in Oxford, see L. Stone (Ed.) The University in Society, Princeton, 1974. The influence of social development in the establishment of scientific discipline has been the subject of some interesting studies: see, for example, B.W.J. Hold, Brit.J.Soc., 1970, 21, 181-199 and references therein.

...the departments of natural knowledge, an elementary acquaintance with which 'ought to be regarded as part of every complete system of education', namely:

First, 'Those which comprehend the knowledge of the general laws common to all matter whatsoever', or 'Natural Philosophy'

Secondly, 'The special properties and relations of those bodies, which are either most familiar to us, most useful, or most generally diffused throughout nature' or 'Chemistry'.¹

It is probable that the young Harcourt would have shared, to one degree or another, this exciting atmosphere at the forefront of British science. The ultimate triumph in establishing a school of natural science at Oxford was to have direct consequences for Harcourt. For without the concerted efforts of these pioneers it seemed likely that students would have left Oxford,

....in utter ignorance of the laws which have been impressed on matter, and unable to explain the commonest phenomena; that he should gaze on the starry heavens without knowing how the motions of the planets are governed..... or..... that he should suppose that

1. Quoted by Harcourt in the 'Oxford Museum and its Founders', Cornhill Magazine, 1910, 352.

earth, air, fire and water are the
four elements of which the world is
composed -

wrote Robert Walker, Professor of Experimental Philosophy
in 1848.¹

Harcourt's career at Oxford began at a time and place
which was to see great and permanent changes, both social
and scientific, in Britain. The Oxford Movement was then at
its height and Harcourt was present, as a student, at the
historic Wilberforce/Huxley debate over Darwin's Origin of
Species which took place in Oxford in 1860.² The struggle
for the establishment of a Science School at Oxford
resulted in the introduction of the Final Honour School of
Natural Science in 1850, only four years before Harcourt
entered Balliol. The first exams were held in 1853.²

Harcourt entered Balliol in 1854, during a period which
was to stand as a watershed for science in Oxford. In one
of the rare records left by Harcourt not dealing directly
with Chemistry, he recalls briefly his own impressions of
those early days,

1 Quoted by Harcourt in 'The Oxford Museum and its Founders,'
Cornhill Magazine, 1910, 359.

2 E.J. Bowen, Chemistry at Oxford, with special reference
to the emergence of physical chemical studies; Balliol
College Library, Oxford (unpublished), Many years later,
when General Secretary of the British Association for
the Advancement of Science, Harcourt recounted this famous
exchange to the biographer of Hooker and Huxley:
O.J.R. Howarth, The British Association for the Advance-
ment of Science: A Retrospect, 1831-1931, London, 1931,
64.

Everything was new and strange, and I may add, delightful to me...It never occurred to me that that was an epoch-making time, when the University was recognising at last the educational value of the natural sciences and was providing for their reception.¹

In his reminiscences, remembering this period of struggle to establish science as a respectable academic discipline, Harcourt commented somewhat drily,

It has been boasted that what Lancashire thinks today England will think tomorrow, and we in Oxford may claim that what England thinks today Oxford will think a few days hence.²

In this he was merely echoing the words of Liebig, doyen of chemistry teachers, who wrote from Giessen in 1851:

That it is a requirement of our times to incorporate the Natural Sciences, as a means of education, into the University Course, is not, perhaps, doubted anywhere except in England.³

1. 'The Oxford Museum and its Founders', Cornhill Magazine, 1910, 356.

2. ibid.

3. Report of the Royal Commission on Oxford, 1852. Similar struggles accompanied the founding of chemistry at Cambridge, the only other major University in England at the beginning of the 19th Century. The Professor of Chemistry at Cambridge in 1852 reported that hitherto the study of chemistry had not only been neglected but discouraged, as diverting the attention of pupils from what was considered their proper academic studies.

It was certainly Harcourt's good fortune that by the time of his arrival at University, the major obstructions which had dogged the efforts of Daubeny and others to establish science at Oxford had been, if not entirely overcome, then at least partially so. Thus he was privileged to move into the University's very first building devoted entirely to the pursuit of chemistry, whilst still an undergraduate. The fight by Harcourt's predecessors at Oxford in the years immediately prior to his entry into the chemical faculty, had been against the rigidity of ancient university structures and the tenacious strongholds of archaic customs. Such battles were not easily won; the establishment of chemistry as a distinct discipline was not totally accomplished even during Harcourt's days nor indeed until much later. Writing as late as 1913, William Tilden in his Progress of Scientific Chemistry in our own Time, commented:

In the ancient universities of Great Britain until quite recent times chemistry has not flourished with the vigour shown by the older studies. We may, however, now look forward hopefully to the day, not far distant, when natural science will be cheerfully and openly admitted to rank in intellectual importance equally with the traditional learning which has come down to us from the past.¹

1. W.A. Tilden, The Progress of Scientific Chemistry in our own time, 1913, London, p.354.

It was a battle in which Harcourt was to partake later in many official capacities, including as President of the Chemical Society. Daubeny, as Professor of Chemistry at Oxford, had reported that the number of students attending chemistry classes had dwindled from an average of thirty-one in the years 1822-1830 to twelve in the period 1838-1851.¹ Almost a quarter of a century later, Harcourt, presiding over the Chemical section of the British Association, decried the lack of students seeking after the excitement and delights of chemical inquiry, 'in a country which abounds in rich and leisurely men and women'.² The proportion of people pursuing original work in chemistry in Britain had remained very small.³ Yet, predictably enough, the establishment of the examination system, which had begun in 1853, had already produced the malaise for the pursuit of success by students in the newly introduced scientific disciplines, 'without enquiring into the truth and consistency of the theories propounded to them'.⁴

1 B.W.G. Holt, op.cit.

2 B.A. Reports (Chem.Sec.) 1875, p. 32-36.

3 The number of chemistry papers published in 1866 in Britain was 127, by 97 authors, compared to 777 papers from Germany (445 authors) and 245 from France (170 authors). In the thirty years or so which spanned Harcourt's chemical career, great changes were to take place in this respect in Britain. By 1897, Harcourt as retiring President of the Chemical Society, reported that part of the Society's problems was now dealing with the number of papers received. (J.Chem.Soc. 1897, 71, 591-594). The membership of the Society was then 2,080. The method adopted for dealing with the volume of papers received was to first take those whose authors were present to read them, in the order in which they were received. The President exercised the power to change the order, should he feel that a communication of special interest warranted it.

4 Reports from Commissions, Scientific Instructors and Advancement of Science, The Devonshire Commission, Vol. 25, 1872.

Science, as an academic discipline, was to remain very much in the lower ranks of educational priorities, both at pre-university level and the research level in Britain for many decades. Benjamin Brodie, directly responsible for Harcourt's introduction into the chemical ranks, was to report in 1872 that the prospect for scientific education faced great difficulties from inadequate preparation at school level and the ignorance of the general public of the importance of scientific knowledge.

These problems were, of course, not restricted to the field of chemical sciences alone. The status occupied by the natural sciences generally remained in a somewhat subordinate position in the eyes of many University members, even many years later, during Harcourt's own Oxford days. H.G. Madan, a close friend and later collaborator with Harcourt on a text book of practical chemistry, recalls that when pictures and objects were being rearranged in his common room, a helpful Fellow, clearly not having had the benefit of scientific instruction, suggested that the chemist's mercury barometer would look far better if hung horizontally instead of vertically.¹

And even among the scientific movement's staunchest supporters, views of the distinct roles of science remained somewhat conservative. Charles Daubeney, credited by many as chief amongst the pioneers of the Oxford Natural Science School, wrote,

¹ Quoted by Harcourt, Cornhill Magazine, 1910, 359.

It would manifestly^{be} quite foreign
to the purpose, and fatal to the genius,
of a school of Physical Science, to
encourage the introduction of any subjects
that are treated mathematically.¹

Daubeny considered that since an independent school already
existed for the instruction of mathematics, there could be
no sensible reason for confusing the two issues, i.e. the
Natural Philosophy of mathematical reasoning and that of the
newly introduced School of Natural Science, including
chemistry.

Fortunately, though Daubeny's wish of seeing the
natural sciences established at Oxford materialised shortly
afterwards, his uncompromising views on the roles of
mathematics and science as distinct disciplines made no
lasting impression. It would be hard to imagine his opinions
on the Chemical Calculus of his successor Benjamin Brodie,
or of the painstaking mathematical calculations of Harcourt
and Esson, which were soon to follow, in the progress of
chemistry at Oxford.

The first scientific building, 'The Oxford Museum', was
founded in 1855, 'with great ceremony' and completed in 1860.
For the first time in Oxford, under one Gothic roof, were to
be found the departments of Astronomy, Geometry, Physics,
Geology, Minerology, Zoology, Physiology, and Anatomy.
Chemistry, however, was apparently in a class of its own -

1 Quoted by Harcourt, Cornhill Magazine, 1910, 357f.

a highly suspect one, for it was literally banished to an annexe. The chemical laboratory was housed in a building which stood alone beside the main museum and was styled after the Abbot's kitchen at Glastonbury Abbey, a design advocated by Ruskin. Though the latter is reported to have waxed lyrical over the beautiful flexibility of the Gothic style for scientific purposes, its utility for chemical research remained in doubt.¹ The first occupant of this new edifice to chemistry was Benjamin Brodie, who took possession in 1857. He was accompanied by the young Harcourt, at that time still an undergraduate.

It is a small irony that, despite the considered opinions of Charles Daubeny, important links between mathematics and chemistry were formed very rapidly at Oxford. The first teacher to be appointed the task of teaching chemistry at Balliol was, paradoxically, the eminent mathematician Henry Stephen Smith,² who had been elected Fellow of Balliol a few years earlier. To fulfill this role, Smith was deputed to take some instructions from Hofmann at the College of Chemistry in London, in 1853.³ Of this period in

1 F.M. Brewer, Chem. and Ind., 1961, 25, 845-853.

2 Henry Stephen Smith, 1826-1883; Smith's mathematical works are assembled in The Collected Mathematical Papers of Henry John Stephen Smith ed. by J.W.L. Glaisher, 2 vols., Oxford, 1894, also Biographical Sketches and Recollections (with Early Letters) of H.J.S. Smith, Oxford, 1894.

3 For accounts of Hofmann's work at the College of Chemistry see Hofmann and Modern Chemistry, J. Science, 1866, 3, 61-78; A.W. Hofmann, A Page of Scientific History: Reminiscences of the early days of the Royal College of Chemistry, J. Science, 1871, 8, 145-153; G.K. Roberts, The Royal College of Chemistry (1845-1853), A Social History of Chemistry in Early Victorian England. Dissertation submitted to the Johns Hopkins University for the Degree of Ph.D., 1973.

Smith's life, not a great deal has been recorded. The training lasted but a few months, a period which was recalled later by his mathematical followers with some trepidation, who saw in this the danger of Smith being diverted from mathematics to chemistry, as Harcourt was to be diverted from classics to the latter. Returning to Oxford, Smith continued his chemical studies with Nevil Story-Maskelyne, Professor of Mineralogy, who instructed him on methods of chemical analysis. The influence of this period of training on Smith, and perhaps ultimately on Harcourt, appears to have been considerable. Smith formed an enduring friendship with Story-Maskelyne, and became so convinced that the properties of elements were connected by mathematical relations that they ought to be capable of discovery by reasoning, in anticipation of experiments.¹

As Professor of Mineralogy, Story-Maskelyne's views on the connections between chemistry and mathematics are interesting. Addressing a meeting of the Royal Institution in 1851, he remarked:

Any facts which can throw light upon the ultimate molecular structure and condition of chemical compounds, cannot fail of possessing interest of a high character, as well for those whose thoughts only casually dwell upon questions of physical science, as for the mathematician and the chemist. To the mathematician, indeed, they would, if completely unfolded, supply

¹ Smith, Henry John Stephen, Dictionary of National Biography Vol 58, 458-461.

the data for him to undertake the resolution of the questions of chemical combination and chemical change, by treating them as problems involving the action of mechanical laws;¹

And (he added), for the chemist, such knowledge would solve some of the most difficult problems of his philosophy. It is notable that Story-Maskelyne saw the resolution of problems of chemical combination and chemical change as tasks primarily for the mathematician. In the same paper, and referring to Biot's experiments with tartaric acid in water, he recalled the controversy between Berthollet and Proust and wrote:

the actions of quantity or mass so dwelt on by the former (Berthollet) are not without a greater significance; and that the power that can thus enable us to determine such important points in chemical statics, is well worthy of the attention of the philosophic mind.²

But ultimately, Story-Maskelyne considered that such knowledge had to be sought amongst the most difficult paths of the whole range of science. From this, it appears that there may have been a certain pattern of continuity between Story-Maskelyne's theory and Harcourt's subsequent ideas. All the problems pertaining to chemical processes mentioned by Story-Maskelyne were later resolved by Harcourt in his

1. Nevil Story-Maskelyne, Notic. of Meetings of R.I., 1851, 45.

2. Nevil Story-Maskelyne, ibid. 49.

study of the complexities surrounding chemical change, on the basis of mechanical laws and the establishment of the mass action law, each with the aid of mathematical analysis. Smith's own original contribution to the field of mathematics was considerable, and he was credited by Jowett and Huxley as having natural abilities greater than those of anyone contemporary with him at Oxford.¹ At Balliol, Harcourt was one of Smith's first two pupils in chemistry. However, the real degree of influence which Smith ultimately had on Harcourt's thinking, which may have tended away from the generally accepted chemical views, towards a mathematical concept, must remain largely conjecture, since no records of Harcourt's early chemistry days appear to have survived. Fifty years later, Harcourt remembered his first chemistry teacher at Oxford with affection, calling him the 'ablest of Oxford Men'.²

Smith was to be only the first Savilian Professor of Geometry with whom Harcourt had close associations at Oxford. The second, without whom little of his life-time's work would have been achieved, as Harcourt readily admitted, was William Esson, his friend and life-long collaborator. His debt to these two mathematical minds are evident throughout his work; his own mathematical skills, though

1. Dictionary of Sci.Biog. Smith, Henry John Stanley, Vol 12, 468.

2. A. Vernon Harcourt, The Oxford Museum, op.cit., 359.

perhaps superior to those of many contemporary chemists,¹ was not commensurate with his needs.² Recalling the period when his other mentor, Benjamin Brodie, invented a new symbolic method of representing the facts of chemistry which was purely mathematical and independent of the atomic hypothesis, Harcourt commented:

I cannot explain the method, for I could never understand it. That was not surprising; but Henry Smith, a great mathematician, could not understand it either; and used to remark pensively - 'depend upon it, you can never get anything out of symbols which you have not first put in'.³

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- 1 Charles Dodgson, a mathematician of considerable skill, counts Harcourt as a 'mathematician' in a diary entry dated 1893: The Diaries of Charles L. Dodgson (British Museum), 21st Dec., 1893: 'Got Professor Clifton's answer to the 'Monkey and Weight' problem. It is very curious, the different views taken by good mathematicians. Price says the weight goes up, with increasing velocity, Clifton and Harcourt that it goes up at the same rate as the monkey, while Sampson says that it goes down!'
 - 2 The lack of mathematical training for chemists was particularly evident during the last half of the 19th Century. Morris Travers in his biography of William Ramsay referred to Ramsay's lack of mathematical competence as the main reason for his not turning to physics; Ramsay later collaborated with the mathematician Rose-Innes on the adiabatics of ether. (Morris W. Travers, A Life of Sir William Ramsay, London, 1956, p. 36). Harcourt frequently referred to his inadequate knowledge of mathematics, and later, when writing to his student John Conroy, advised the latter to take up mathematics; 'I remember Esson assuring me that I should like the differential calculus if I would only work at it a bit'. (Conroy Papers, Balliol College Library). More revealing, Harcourt also wrote that he was unable to see the true significance of the temperature/rate expression in one of his own major publication, which was also his last.
 - 3 A. Vernon Harcourt, ibid. 362.

Smith's words clearly had considerable impact on Harcourt; his work with Esson never contained more mathematical symbols than was imperative. The continued well-being of the newly established Chemistry Department also owed much to Smith's powers of skilful advocacy, for he constantly pleaded its cause for fresh grants to Convocation, in place of the Professor of Chemistry, Benjamin Brodie.¹

Brodie, whose father was the famous surgeon of the same name, Sir Benjamin Brodie, succeeded Daubeny as Professor of Chemistry in 1855, the year in which construction of the Oxford Museum began. For the next two years, Brodie was to join with Smith in the cellar laboratories of Balliol, awaiting the completion of the new science building.² In retrospect, Brodie is probably best remembered for his attempts to introduce a revolutionary new approach, the chemical calculus. By 1867, when Brodie presented his ideas to the Chemical Society, he had become convinced that Dalton's atomic hypothesis was no longer adequate to deal with the complicated system of chemical facts then emerging. He proposed a theory which required no hypothesis on the nature of matter, but in which new symbols were defined to represent chemical operations in space.³

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1. Brodie was forbidden to enter the Convocation House because of his refusal to sign the 39 Articles.
 2. E.J. Bowen, Chemistry in Britain, 1965, I, 517-520; H. Hartley, ibid., 521-524; J. Roy. Inst. Chem., 1955, 79, 118-127. F.M. Brewer, Chem., and Ind., 1961, 845-853.
 3. Phil. Trans., 1866, 156, 781-859; Chem. News, 1867, 15, 295-305.

That Brodie's ideas were not well understood at that time, nor indeed afterwards, is fairly evident.¹ Even though William Crookes introduced Brodie's paper at the time as 'the chemistry of the future', Brodie himself described the subject as 'somewhat abstruse and difficult'.² But what it did achieve for the chemical community was great debate and controversy, in the midst of which loomed the fundamental question of the relevance of the atomic theory of matter to chemists. It was a debate in which physicists were to play a major role, as we have seen.

Among the eminent physicists present when Brodie delivered his ideas to the Chemical Society³ was Clerk Maxwell, who confessed that his feelings received a whole-some shock from two of the statements in the diagrams - first, that space was a chemical substance, and second, that hydrogen and mercury were operations.⁴ Maxwell went on to say that in order to decide with certainty the reliability of the atomic theory, it would be necessary to consider the problem from a dynamic point of view. He was, presumably, referring to the reaction of chemists, for the kinetic theory of matter was already then well established amongst physicists. Brodie also saw the significance of this, for on the same occasion, replying to the reactions of his audience, he said:

1. E.J. Bowen, Chemistry at Oxford, Balliol College Library, (unpublished).

2. Chem. News, 1867, 15, 295.

3. Chem. News, 1867, 15, 303.

4. ibid., 303.

I think, that the object of a method is not simply to give us statical formulae, but that we must also consider the dynamics of the science. I mean, by 'statical formulae', that we are not merely to consider what matter is, but that we are to consider the laws also by which matter changes.¹

The year of this controversy was 1867. But seventeen years previously, Brodie had already been considering related problems, at a time when the atomic theory did not appear to him an anathema. In 1850, he had published a lengthy paper entitled, 'On the Conditions of Certain Elements at the Moment of Chemical Change' in which he considered philosophically, but on the basis of exhaustive experiments, what may have been the beginnings of observations on the actual process of chemical change.² He proposed several 'mechanisms' by which chemical action might be propagated, to explain such well-known phenomena as the slow reaction of Zinc with hot concentrated potash solution. Brodie deduced that it was the quantitative relation between the decomposing substances which was essential - and these could only be determined experimentally.³ Most importantly, he considered that it was quite possible that this action varied according to some other, as yet unknown, chemical law, even though:

It might have none of the character of a

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1. Chem. News, 1867, 15, 305
 2. Phil. Trans., 1850, 2, 759-804
 3. ibid., 775

chemical change; it might, for example, vary directly with the acting masses, or with the temperature alone, or be a function, so to say, of so many variables that the true law of action would be altogether hidden.¹

Much of Brodie's work involved the peroxides, notably those of barium and hydrogen, and as Harcourt later recalled, explosions and shattered glass were frequent in those days.²

These investigations appear to have been the last serious experimental work which Brodie undertook between 1862 until his death in 1880. His energies were, presumably channeled into developing the chemical calculus. Of his mentor, Harcourt later wrote:

Brodie's lectures and research were alike excellent. He was a man of great originality and wide range of interests, an indefatigable worker at chemical problems. Unfortunately ^{at this time} he read Boole's 'logic' which inspired him with a desire to invent a new symbolic method of representing the facts of chemistry ... But I'm afraid he was saddened by the non-reception of his ideas and it partly withdrew him from the experimental work in which he excelled.³

As in the case of Henry Smith, it is difficult to

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1. Phil. Trans., 1850, 2, 759-804
 2. Cornhill Magazine, 1910, 361
 3. Cornhill Magazine, 1910, 3, 61-362

assess the degree to which Brodie actually influenced Harcourt's subsequent chemical ideas, apart from the obvious fact that Brodie's chemical calculus made no impact on him at all. But if Harcourt's principal work was not directly influenced by Brodie, some patterns are also evident. Thus his initial research interests were traditionally those of his mentor, and one of Harcourt's first papers was on the peroxides of potassium and sodium.¹ For Harcourt, all the substances on which he and Esson were later to do their analysis, iodine, peroxides and chromates were familiar ones in Brodie's laboratory. This was to have distinct advantages over the solid phases chosen by the Norwegians Guldberg and Waage in similar investigations. To Brodie, too, may be due the training in those early years of prolonged thoroughness and refinement of experimental techniques which has made Harcourt and Esson's work unique. Outside the confines of the chemical laboratory, Harcourt's early Oxford days were obviously marked by friendship with the Brodie family. Together with his close friend Charles Dodgson, Harcourt took frequent river trips accompanied by the Brodie children, trips which evoke scenes later described in Dodgson's diaries, now in the British Museum.²

(b) The Course of Chemical Change and Other Inventions

The young Harcourt was clearly an excellent student,

1. J. Chem. Soc., 1862, 14, 267

2. See The Diaries of Charles Dodgson, Brit. Museum, London

for in 1858 Brodie appointed him as lecture assistant in the brand new chemical laboratories of the Oxford Museum. This was something of an honour for one as yet ungraduated, but he achieved this a year later with a First Class in the School of Natural Science and became Demonstrator in the students' laboratory. Within a year of this, Harcourt applied, together with two other candidates, for the position of Lee's Reader in Chemistry, which was also to have an associated senior studentship, but which did not call for ordination. The examination included a practical test which required the candidate to improvise an apparatus for the procurement of nitrogen from the atmosphere.¹ Harcourt succeeded, and became both Lee's Reader and Senior Student (i.e. a Fellow) of Christ Church, positions which he held until the end of his Oxford days. It was around this time, 1859, that Harcourt began his work on the rates of chemical change, which were also to last a life-time. The chemical significance of this work will be discussed in the next section.

Harcourt, with considerable foresight, sought for explanations of chemical change in the foundations of mechanical laws from the earliest stages of his work. To achieve this, Harcourt was fortunate in having the life-long collaboration and friendship of the mathematician William Esson. It is no exaggeration or conjecture to say that without this partnership, Harcourt's work would not have

1. The Commemoration Oration of 1969; Augustus George Vernon Harcourt, F.R.S., by Adam Scott. Unpublished paper, Christ Church Library, Oxford.

succeeded as it did. This, Harcourt frequently and gratefully acknowledged. In a letter to Sir John Conroy, a former student but later close family friend, dated September, 1894, Harcourt wrote:

My chief occupation has been finishing a paper which ought to have been finished twenty and more years ago: I have finished it now, except a possible summary, and have sent it off to Esson for correction and approval, the former being especially required by my efforts at algebraic or graphic representations.

He continues:

I think the paper of the work described rather good - it was so long ago I can almost judge of it from outside, - but much the best bit is Esson's description of our temperature experiments.¹

Harcourt's appreciation of Esson's contribution to their efforts is constant. Almost eighteen years later, writing to the Secretary of the Royal Society, he said:

I enclose herewith my account of some recent observations of the rate of a chemical change at different temperatures, and with it an appendix or paper by Esson dealing with my figures and those of many other writers. I suggested to him that

1. Conroy Papers, I. B. Bundle 14, Balliol College Library, Oxford

as his contribution is of much larger scope than mine, it ought to appear as the principal paper and mine might follow as a recent piece of work, communicated to him in M.S. (manuscript), of the kind which he discusses.¹

William Esson (1839-1916) matriculated from St. John's College, Oxford, in 1855 with a First in Mathematics at the very early age of seventeen.² Although the paths which brought Harcourt and Esson together at Oxford appear to be quite different, they appeared to have shared many similar characteristics. Though Esson was a few years junior to Harcourt, they were elected Fellows (Esson to Merton College) within a short time of each other, and also married in the same year, 1872.³ According to the accounts of their pupils, both carried out their roles as teachers superbly well; their dedication and heuristic methods of teaching, to the great benefit of their students, are equally echoed by two grateful recipients; both accounts say that by their examples, the teaching at Oxford, not least in chemistry and mathematics, was raised to a new level of inspiration and care.⁴

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1. The Library, Royal Society. It is not clear whether these two letters refer to the same piece of research; the eighteen year lag is puzzling, although the publication of their paper dealing with the variation of rate constants with temperature in 1912 was their last major publication together.
 2. Proc. Roy. Soc., 1917, 93, liv-lvii.
 3. Before that year, Fellows at Merton were required to vacate their Fellowship on marriage. ibid. lv.
 4. Esson, ibid.; Harcourt, Proc. Roy. Soc., 1920, 97, vii-xi.

Esson's close collaboration with Harcourt is clearly evident up to their last paper together, published in 1912, only four years before Esson's death. Of their initial meeting there is no record, but it appears that in his early years at Oxford, Esson had shown considerable interest in experimental chemistry and had worked as Chemical Demonstrator to Harcourt.¹ This would indicate a very early acquaintance, begun probably when Harcourt was about to take up his Lee Readership. The fortuitously early meeting of mathematical prowess and experimental expertise at the very conception of what was to become a new school of chemical thought may explain the familiarity with which each appeared, effortlessly, to communicate with the other in the theoretical interpretation of their results. It is for the fruits of this collaboration with Harcourt that Esson is most lauded by his mathematical contemporaries; for Esson, though Savillian Professor of Geometry from 1897, wrote little on his own subject.² Of these years of labour with Harcourt, a later Fellow of the Royal Society, formerly Esson's pupil, was to write:

Harcourt began a research on the conditions of chemical change, and invited Esson to join him in the investigation. Shoulder to shoulder they worked together for years, Harcourt planning the experiments, both attending to every detail and checking one another's observation of time intervals,

1. F. Szabadváry, Dictionary of Scientific Biography, Vol. 4, 411

2. Proc. Roy. Soc., 1917, 93, liv-lvii

Esson doing the calculations. These established to the hilt the accuracy of the law that, in unit volume of a dilute solution at constant temperature, the rate of chemical change varies directly with the mass of each of the interacting substances. It was pioneer work, and secured sure, if not speedy, recognition as novel and general in character, flawless in execution, and mathematically sound. Its method prevails till this day.¹

Even allowing for devotion to a former mentor, these words summarize well the relationship and work of Harcourt and Esson, seen from a mathematical rather than chemical vantage. Harcourt also initiated a considerable interest and understanding of the properties of gases, during his years at Oxford; this was to be perpetuated by the research on rate studies of explosion of gases by his pupil Harold Dixon. In 1872, Harcourt was appointed one of the three Metropolitan Gas Referees who were responsible for testing the safety and levels of purity of coal gas used in London.

Much less well known than either his work on rates of reaction of solutions or gases was his considerable flair

1. Proc. Roy. Soc., 1917, 93, liv-lvii

for inventions, both at work and leisure.¹ Harcourt was responsible for the introduction of the pentane lamp which came to replace the spermaceti candle as the official standard of light.² Between the years 1899 and 1911, Harcourt worked on the administration of chloroform as an anaesthetic, testing it on himself, his family and frequent guests, much to their chagrin. Earlier he had successfully devised a method for quantitative determination of chloroform by its conversion, when mixed with air, to carbon dioxide and hydrogen chloride in the presence of red-hot platinum wire and steam. This was utilised when The British Medical Association adopted Harcourt's Inhaler as satisfying the minimum dose which would secure anaesthesia during operations without endangering life.³

(c) Chemist and Teacher

Though few personal or unpublished papers appear to have survived,⁴ all the evidence which emerges from a study

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1. This aspect of Harcourt's character gave rise to speculations by many of his contemporaries and by his family that he was, in fact, the original model for the White Knight of Alice Through the Looking Glass, who was very fond of inventing things - see next section.
 2. Proc. Roy. Soc., 1920, 97, vii.
 3. Proc. Roy. Soc., 1920, 97, x.
 4. There are a number of personal letters written by Harcourt including one to his parents when he was eight years old, in the family possession.

of Augustus Vernon Harcourt suggest that he was a man of considerable originality of thought, a careful thinker, an experimenter of unquestionable skill and tenacity, and a truly gifted teacher of chemistry. More importantly, his work laid the foundation for a new school of physical chemistry, a continuity which can be traced to contemporary Oxford chemists. Recognition of his gifts during his lifetime was not lacking, though varied. Beginning with the teaching of chemistry to a future King of England whilst he himself was barely graduated,¹ he became F.R.S. in 1868, serving on its Council and as frequent referee, President of the Chemical Society, President of the British Association, and held Honorary Doctorate Degrees from Oxford, McGill, and Durham Universities.² As we have seen, he also distinguished himself in two other totally unassociated fields - on the Gas Board and on the Council of the British Medical Association. He appears to have been liberal in both private life, as accounted personally by his daughter (one of ten children) and politics (his wife, Rachel Mary Bruce was the daughter of the Home Secretary H. A. Bruce in Gladstone's first administration). His father, Admiral Frederick Vernon Harcourt, veered towards Lowchurch doctrines and left records of his deep Christian commitment in several sermons.³ These influences played a considerable

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1. Among Harcourt's first pupils after his appointment as Demonstrator was the Prince of Wales, afterwards Edward VII.
 2. Proc. Roy. Soc., 1920, 97, x
 3. Admiral F. Vernon Harcourt, Archives of the British Museum. These strong early religious influences were to make Harcourt veer towards atheism in adult life.

part in formulating the style of life which Harcourt led at Oxford. Harold Dixon, who knew him first as teacher and later in the role of Professor of Chemistry at Manchester, himself an eminent chemist, gratefully acknowledged his debt to Harcourt and wrote:

Of the painstaking character of Harcourt's demonstrations...of the patience and personal trouble he took with each beginner, generations of old Christ Church men can speak with grateful appreciation. The minutiae of manipulation appealed to him, but they were only means to attack the largest problems; for him no defect was too small to remedy, no authority was too great to question... Few men have been so completely happy in their work, or lived so much in the lives of their students.¹

Another of his students who was to continue the tradition of physical-chemical research at Oxford was Sir John Conroy. Amongst the few records remaining of Harcourt's life are the series of letters to Conroy, who became a life-long friend.² To Conroy, Harcourt frequently offered advice and outlined new scientific ideas which constantly occurred to him. Writing in 1875 to Conroy, Harcourt said:

There is a great field most imperfectly explored and I should rather say hardly

1. Proc. Roy. Soc., 1920, 97, xix, xi

2. The Conroy Papers, Balliol College Library

entered upon in the optical examination of different substances. It is to such examination that one must look for information as to the structure of molecules and the causes of the differences - sometimes the fact of the differences between isomeric compounds.¹

The important role which Harcourt played in the establishment of chemistry at Oxford has been noted by several chemists in recent times. Harold Hartley, in his account of Oxford College Laboratories, wrote:

Augustus Vernon Harcourt, one of Henry Smith's first two pupils, was destined to be the key figure in the development of teaching and research in college laboratories, as five of his pupils were elected into the Royal Society and the successive generations of their pupils provided nearly all the heads of College Laboratories, besides contributing many other distinguished teachers of chemistry. I was made to realise the strength of the Harcourt tradition when my tutor, Sir John Conroy, saw me commit one of the minor crimes of the laboratory.

1. The Conroy Papers, Balliol College Library.

He looked at me sadly; and all he said was: Harcourt would have told Dixon, Dixon would have told Baker and Baker would have told you.¹

F. M. Brewer, Reader in the Chemistry department in 1948 wrote more strongly:

Vernon Harcourt's work at Christ Church produced a number of distinguished chemists who themselves contributed later to the building up of the chemistry school in all its branches... By contrast, the two Professors, Brodie and Odling, who held the Chair of Chemistry until 1913, have left no great heritage behind.....²

The reference to Brodie and Odling is relevant to Harcourt's chemical career at Oxford, which, long as it was, remained in the shadows of the administration of these two figures. Brodie retired as Professor of Chemistry in 1872 and was succeeded by William Odling (1829-1921), who held the chair for a record of forty years, until his retirement in 1912. Of these long years, during which the physical sciences at Oxford were reputed to have reached a record low, it has been said:

Odling appears to have been the perfect scientific anti-hero, holding a vital chair for an unconscionable long time,

1. H. Hartley, Chem. In Brit., 1965, I, 532

2. F. M. Brewer, Chemistry at Oxford, The Oxonian, 1948, 99.

but doing nothing. He led no research, published hardly any work after his election, and the very university in which he spent over half an exceptionally long life has been glad to forget him.¹

Yet before his election to the Oxford Chair, Odling was numbered amongst the handful of leading British chemists.² The question as to why Harcourt did not succeed Brodie naturally arises, since by then he had certainly proved himself an able teacher and chemist. It is not known whether the question arose at the time of election; Odling was certainly the far better known figure, nationally. He had succeeded Michael Faraday as Fullerian Professor at the Royal Institution in 1868 and was an eminent member of the Chemical Society, of which he was Secretary for thirteen years and an active contributor between 1860-1875. Harcourt, in contrast, remained very much an Oxford figure throughout his career; it is fairly certain that the significance of his chemical ideas, and the mathematical analysis by Esson, were not, at that time, well understood by contemporary chemists, nor indeed for a long time afterwards.

Amidst the emerging picture of Harcourt as a leading chemist in the scientific echelons of Oxford academic life, several puzzling factors remain. Despite his very evident abilities, he appears to have played no part in the most

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1. P. J. Freeman, The Life and Times of William Odling, BSc. Thesis, Oxford University, 1963, 5-6.
 2. W. H. Brock, in C.C. Gillespie (Ed.), Dictionary of Scientific Biography, Vol. 10, 177-179.

controversial chemical issue of his day - the atomic debate, a debate in which his mentor, Benjamin Brodie was becoming 'a cat among the chemical pigeons'. Brodie, who was clearly familiar with the new ideas of reaction mechanics afforded by Harcourt and Esson's work, was unable to reconcile these ideas with the atomic theory. If anything, Harcourt's sympathies were with Williamson¹ but it is not in the least evident that he made any special efforts towards the elucidation of this fundamentally important question. Only in his last address to the Chemical Society as President, in 1897, did he put on record some of his thoughts relating to the matter.

Almost more puzzling to anyone endeavouring to bring together a sketch of Harcourt's life and work is the total lack of indication, in his major papers, that he was aware of the work and ideas of his contemporaries, in particular those of Guldberg and Waage in Norway. As will be shown later, the work and ideas of Harcourt and Esson bore many similarities with those of their fellow workers in Norway, though it must be pointed out that there is no indication that either team was initially inspired by the work of the other. Near the beginning of his work, Harcourt certainly was not aware of any results published by the Norwegians. For in 1867 he wrote, "At present such knowledge as we possess of the course of chemical changes, and of their relations to the conditions under which they occur, is merely qualitative".² That each became aware of the other's

1. Adam Scott: op. cit. , 9

2. J. Chem. Soc. 1867, 20, 460

work, in time, there can be no reasonable doubt. William Ramsay, who was an admirer of Waage, was also a personal friend of Harcourt. In the summer of 1889, Ramsay spent much time with Harcourt's family and it seems unlikely that he would not have discussed with Harcourt the ideas of the Norwegians, whose work was evidently familiar to him. Ten years previously, in 1879, Ramsay had made a special trip to meet Peter Waage in Christiania and failed. On a following visit, one of his first missions on arriving at Christiania was to call again on Waage with whom he spent a full and congenial day in the country, followed by a visit to the latter's laboratory the next day.¹ Several biographies testify to the exceptional abilities and personality of Ramsay, both as chemist and as a member of the chemical community.² Ramsay's personality, it has been said, irradiated contemporary British chemistry³ and at least one of his major discoveries was communicated to the Chemical Society by Harcourt personally, with whom he shared great experimental skills. With his intellectual insights and close contacts with both Harcourt and Waage, it seems wholly unlikely that either party was not made fully aware of the connotations of the other's ideas. On the similarity and differences of their work, more will be said later. Had there not been this personal link by Ramsay between the work at Oxford and Christiania, some doubts may exist as to

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1. Morris W. Travers; A Life of Sir William Ramsay, London, 1956, 50, 97.
 2. Several biographies of Ramsay have been written, notably those by Travers, W. A. Tilden; see ref. in Travers.
 3. T. S. Moore, J. C. Philip, The Chemical Society 1841-1941 A historical review, London, 1947, 99.

how widely available were their chemical papers, complicated perhaps by a lack of verbal communication. Certainly, Guldberg and Waage, whose original paper was published in their native language, many years later republished it in French, the most common chemical language of the day. On Ramsay's visit to Norway, Waage and he communicated in German, a language which Ramsay knew well from his student days at Tübingen.¹ Harcourt, unlike many of the leading British chemists of the day, did not spend any period of his training abroad. His attitudes may thus have differed from that of, say, Ramsay. A clue to these slightly puzzling aspects of Harcourt's work and nature may perhaps be found in the words of a later Vice-President of the Chemical Society; Tom Moore, in his historical review wrote:

He (Vernon Harcourt) appears to have been a man who showed at his best in official positions. As President (of the Chemical Society) he was universally liked.....

He is said to have discharged his duties as a Secretary of the British Association for fourteen years with conspicuous tact. He was, perhaps, not always equally tactful with his pupils. The remarkable ability and originality of his scientific work might well have had a wider influence, if he had been more in touch with other workers in the same field.²

1. Travers, op. cit.

2. T. S. Moore, J. C. Philip, ibid., 81.

This last observation is particularly interesting, in view of the subsequent influence and impact of Harcourt and Esson's work on the development of chemistry, as will emerge later. But of Harcourt's personal influence, especially on the younger members of the Chemical community, there is ample evidence; Sir Martin Forster, elected Fellow of the Chemical Society in the early eighteen-nineties, and subsequently Vice-President, wrote:

The type(of president) changed with Vernon Harcourt, whom we on the back bench dearly loved. His appearance and Presidential mien were impeccable, and long sentences were as precious to him as to Henry James; but he swayed them with equal skill and we would sigh with relief when the soothing and beautifully modulated voice emerged successfully from a seemingly hopeless tangle.¹

At the centre of this chemical scenario, it is the larger, social and domestic aspect of Harcourt's life which perhaps dominated the path of his career. Blessed with a highly contented and prosperous family life, the large and imaginatively designed house Harcourt built on the edge of the river Cherwell stands today as a testimony to those

1. M. O. Forster, Chemical Changes and Chances, The Twentieth Streatfield Memorial Lecture, R.I.C. 1937.

bygone days.¹

The portrait of Harcourt which emerges is that of an equable and diplomatic figure, persistent rather than revolutionary in his chemical beliefs, with exacting, perhaps unbending standards. At least one contemporary chemist suffered considerably under this attitude.

In 1871, a lengthy paper by Edmund J. Mills, entitled "On the Chemical Activity of Nitrates" was sent by the Secretary of the Royal Society, G. G. Stokes, to Harcourt requesting him to act as referee. In a carefully considered reply to Stokes, Harcourt wrote:

In conclusion, it would seem that this paper, though it contains records of some excellent experimental work, is marred by the theories which the author endeavours, with much ingenuity, to support upon a quite insufficient basis of facts. As far as my judgement goes, this paper is not suitable for publication in the Philosophical Transactions.²

Mills did not accept this judgement with good grace, and protested strongly in a letter to Stokes:

- but now the very purpose of my paper
has been mistaken, and that by a referee

1. Harcourt's only surviving child, whose father died when she was still very young, recalls that he was an extremely strict, though loving, father. The beautiful house and grounds of the Harcourt home now form part of St. Hilda's College.

2. Roy. Soc. Library, RR7, 113.

who cannot write his own equations accurately. I may add that he is known to me... never before have I been so annoyed and hurt, and powerless.¹

In 1882, Mills again had his work refereed by Harcourt, whose insistence on experimental accuracy and rigour was, to judge by his own work, quite exceptionally high and who clearly demanded the same of others. Replying once more to Stokes, Harcourt wrote:

...the figures obtained seemed to be dependent upon the conditions of the experiment, strength of solutions, the time during which the reagents were left in contact, and the temperature... what reason is there to believe that if these conditions had been different, the contents of the equations calculated or numerical coincidences observed would have been the same? As far as I can judge these experiments prove nothing and do not establish any definite facts which could be of service in connection with any further investigations...(whether it is of) any value in mathematical description I am not competent to say.²

1. Roy. Soc. Library, RR7, 115, 116.

2. Roy. Soc. Library, RR7, 115/116.

We have already seen the role which Mills played in the chemical drama surrounding the atomic debates.¹ His approach to these and other chemical phenomena appears to have become increasingly metaphysical in later years. Although Stokes was reconciliatory in turning down Mills' contribution to the Proceedings, suggesting alternatives, the latter considered that the rejection amounted to a permanent blot on his chemical career.²

Harcourt's philosophy of stringent analysis as a first principle in scientific method is amply borne out from his first paper and in each subsequent publication. To his students too, he advocated the same approach:

The evil of being anticipated (by the industrious German) is much less than that of making statements which you or others afterwards discover to be inexact, or even that of making a doubting utterance in a matter in which a little further enquiry must plainly lead to certainty,³

He wrote to Conroy in 1873. This attitude was to be retained in his criticism of all scientific work which came his way. Though not referring to Mills' work specifically, Harcourt held strong views on the need for accuracy in quantitative

1. See earlier section on Dynamic Chemistry.

2. Roy. Soc. Library, RR7, 115/116.

3. Conroy Papers, Balliol College Library, Oxford, Box II.

measurements in chemistry:

The general condition - he wrote in 1881 - which a subject worth working at in chemistry and physics needs to satisfy are that it should be capable of yielding exact (that is, within 1 to $\frac{1}{2}$ % error) quantitative results under conditions all of which are determinate within the same limit of error. I feel sure that much chemical work is all but useless because the worker has not determined or even observed or thought of, some of the conditions on which his results depend.¹

Yet, in spite of his progressive ideas on the quantification of chemistry, Harcourt remained somewhat conservative on other chemical matters, unconvinced by the later theories of solution and ionisation and refusing to reconcile his ideas of chemical change with concepts of dissociation and decomposition.

Nevertheless, many of his ideas and chemical theories were among the most advanced of his day, and established the concept of chemical velocity as a distinct form of study. The work of Harcourt and Esson spanned a remarkable forty-seven years, beginning with their first publication in the Royal Society Proceedings of 1865 and ending with the publication of their Rate/Temperature paper in 1912. To

1. Conroy Papers, Balliol College Library, Oxford.

these studies of chemical change and the concept of time incorporated in these changes, we shall shortly turn, after a brief literary digression.

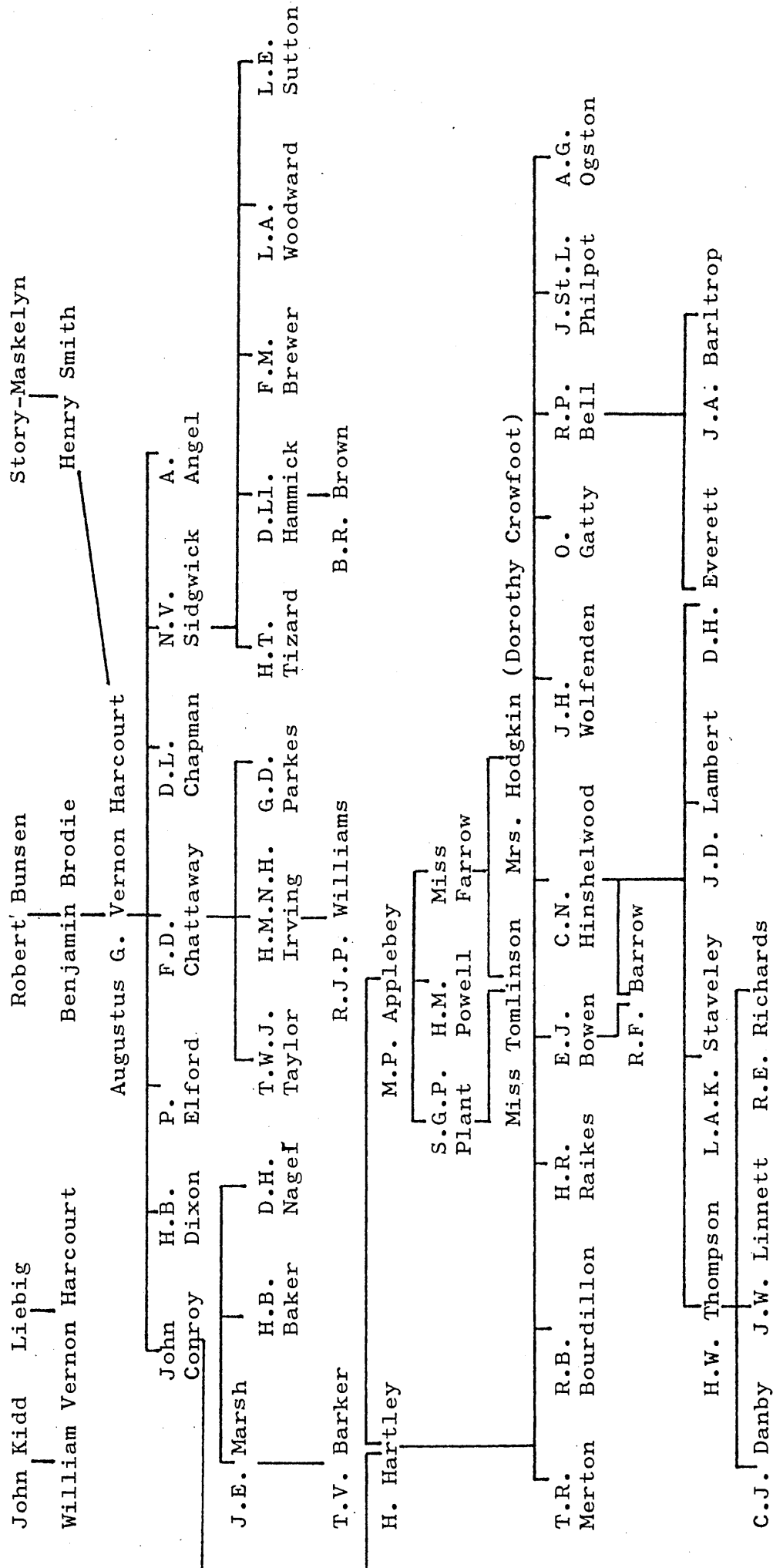
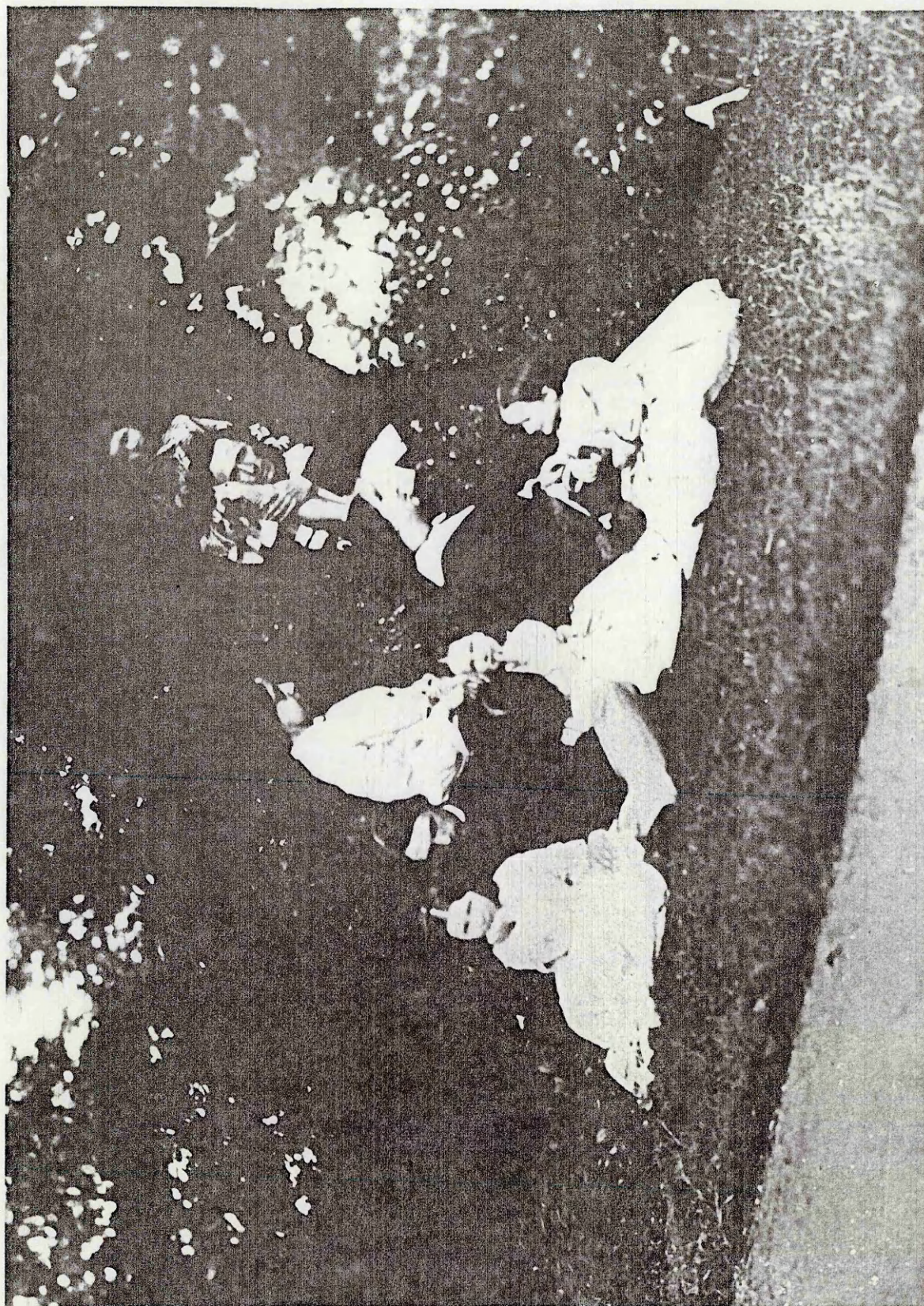


Table from: H. Hartley, J. Roy. Inst. of Chem., March, 1955, p. 125, showing the relationships between A. G. Vernon Harcourt, his teachers and pupils.



Oxford days; the young Harcourt with Professor Sir Benjamin Brodie and his family

(d) Chemistry's White Knight: A Literary Digression

Amongst the most interesting aspects of Harcourt's long career at Oxford was his friendship with Charles Dodgson, fellow member of Christ Church and author (as Lewis Carroll) of the immortalised Alice Tales. Dodgson entered Christ Church in 1851, three years before Harcourt came to Oxford. The number of entries in Dodgson's diaries, now in the British Museum, dating from 1855 to just before his death in 1898, show clearly how frequently they spent time together, and with other Oxford figures like the Brodies and the Liddells.

Sir Benjamin Brodie was then Professor of chemistry at Oxford and Harcourt's mentor, and Alice Liddell was the young daughter of the Dean of Christ Church. During the first week of August, 1862, the diaries indicate that Dodgson and Harcourt had spent much of their free time together with the Brodie and Liddell children.

August 1st 1862,

As the Dean's children are still here, Harcourt and I went over to see if they could come on the river today or tomorrow, and remained a short time
.....

August 2nd 1862,

Mrs Brodie brought her children over to be photographed in the morning after which Margaret and Ida (the Brodie children) came down again to go with the Liddells, Harcourt and myself, on the water. Then back to croquet at the Deanery, and Harcourt

and I went there again after dinner to escort the Brodie's home, the Liddells also insisting on walking there and back with us

August 5th 1862,

After dinner, Harcourt and I went to the Deanery to arrange about the river tomorrow, and stayed to play a game of "Ways and Means" with the children

It was around this time that the tales of Alice were born, for Dodgson wrote,

6 August 1862,

In the afternoon, Harcourt and I took the three Liddells up to Godstow, where we had tea: we tried the game of "The Ural Mountains" on the way, but it did not prove very successful and I had to go on with my interminable fairy tales of Alice's adventures. We got back soon after eight, and had supper in my rooms, the children coming over for a short-while - a very enjoyable expedition

To generations of Alice fans, one of the mysteries surrounding the creation of Carroll's tales is the contradicting memories of a hot summer's day, as remembered by Alice herself many years later - and recorded in the opening lines of the famous tale: All in the golden afternoon, full leasurely we glide, and the discovery that the weather, that particular day, Friday

July 4th, near Oxford was 'cool and rather wet', an unlikely occasion for the inspiration of such nostalgic happiness.¹ It may be, perhaps, that it was this later trip to Godstow, with Harcourt and the Liddell children, that later memories were to recall. The diaries also record several other river trips to Nuneham, the home of Harcourt's uncle, William Vernon Harcourt, for tea. Alice Liddell, recalling the event in later years, wrote:

Most of Mr. Dodgson's stories were told to us on river expeditions to Nuneham or Godstow, near Oxford I believe the beginning of Alice was told one summer's afternoon when the sun was so burning hot that we had landed in the meadows down the river, deserting the boat to take refuge²

W.H. Auden has called the golden afternoon on which Alice's adventures were first inspired, purported to be 4th July, "as memorable a day in the history of literature as it is in American history". Perchance for the history of literature that, in fact, it was August 6th 1862 that Dodgson was to recall many years later with the poignant words:

1. Recorded in Helmut Gernsheim's Lewis Carroll: Photographer and commented upon by Martin Gardner in The Annotated Alice, Penguin, 1965. See also: Caryl Hargreaves, The Cornhill Magazine, July, 1932.

2. S. Collingwood, The Life and Letters of Lewis Carroll.

A tale begun in other days,
 When summer suns were glowing
 A simple chime, that served to time
 The rhythm of our rowing -
 Whose echoes live in memory yet,
 Though envious years would say forget.

With the publication of Alice Through the Looking Glass in 1871, however, the envious years were to bring the opposite - the tales begun in other days became etched upon the memories of millions.

But the link between Harcourt, Dodgson and Alice is a closer one than that they merely knew each other. Enthusiasts of the Dodgson tales have always accepted that the characters in the Alice books relate to personalities associated with real lives in 19th century Oxford, though Dodgson no doubt took some care to disguise the more irreverent of his caricatures. Surrounded as they were by the most select of the University dons, as well as many notables of the day, including the Prince of Wales, Dean Liddell's children must have spent many an enjoyable hour matching the story-book characters with those they knew. The Red Queen in Through the Looking Glass, for instance, was probably the Liddell children's governess, Miss Prickett, known as 'Pricks', because she was one of the 'thorny' kind.¹

The story, still told in Oxford scientific circles

1. The Annotated Alice, op.cit.

today, is that the White Knight's flair for invention, as recounted in Through the Looking Glass, was a reflection on Harcourt, who was, without a doubt, a highly innovative and successful inventor, as we have seen earlier. His family was also the recipient of several of his inventive ideas. At his home in Oxford, which he built over the River Cherwell, and which he reached conveniently by means of a punt, Harcourt built a squash-court, which doubled as a ball-room when the occasion called. For his children, of whom there were eleven, he built a hard, out-door, tennis court, which, in the winter, could be flooded with water to form an ice-rink. His family still recalls how Harcourt attempted to apply logic to their domestic economy, including the building of a special fire-place. This was high though not very deep, and the coke was laid in layers separated by metal and asbestos plates. On the top of this was laid the ordinary firewood, and when lit, the fire would burn like a time-piece, exposing each layer in turn. In front of this fireplace, which closely resembles the Tenniel illustration of Alice's Looking Glass fire-place, the children would hold his letters, written in invisible ink, and thrill to see the contents exposed.¹

Dodgson himself was also fond of inventing things, as many writers have pointed out.² Among the inventions which Dodgson talks of, are a travelling chess set, with

1. Recalled by Harcourt's daughter, Mrs Schiele, 1979.

2. See The Annotated Alice, op.cit.

holes to hold the pegged pieces, and countless games and toys for his many young friends. He also shared many of his inventive interests, such as photography, with his friend Harcourt. Dodgson who was a remarkably gifted photographer, depended on Harcourt for much early assistance, as this previously unpublished letter shows:¹

Mar. 5th/72

O come to me at two to-day
 Harcourt, come to me!
 And show me how my dark room may
 Illuminated be,
 Though gondolas may lightly glide
 For me, unless you come,
 No friend remains but cyanide
 Of pale potassium!

Though maidens sing sweet Barcaroles
 (Whatever they may be)
 To captivate Lee's Readers' souls,
 Yet Harcourt, come to me!
 Yes, come to me at two today
 Or else at two tomorrow,
 Nor leave thy friend to pine away
 In photographic sorrow.

C.L.D.

1. Unpublished letter from Dodgson to Harcourt in the possession of Robert Vernon Harcourt, grandson of Augustus V. Harcourt.

Dodgson and Harcourt were also, sometimes, competitors for inventions. In his diaries of 1871, Dodgson wrote:

Nov. 22nd,

The cards (were) deemed to be a success and won much praise (I find Harcourt believes them to be his invention also. My record, May 12, written May 22 looks as if I then believed it to be mine. I cannot now remember, and it matters little which is right.)

Commonly, scholars of Dodgson's work believe that the White Knight is, in fact, a caricature of Dodgson himself, not only because of his obvious knack for inventions but because of the special relationship between the Knight and Alice. As Martin Gardner points out in his Annotated Alice, for instance, of all the characters Alice meets in her two dream adventures, only the White Knight seems to be genuinely fond of her and to offer her special assistance. The Knight is also the figure that Alice herself remembers best in retrospect:

Of all the strange things that Alice saw in her journey Through the Looking Glass, this was the one she always remembered most clearly. Years afterwards she could bring back again as if it were yesterday - the mild blue eyes and kindly smile of the Knight, the setting sun gleaming through his hair, and shining on his

armour in a blaze of light that quite dazzled
her¹

Dodgson wrote in a letter that the character of the White Knight - "whose hair was whiter than the snow, whose face was very like a crow, with eyes, like cinders, all aglow" - was meant to suit the speaker in the poem itself, and who was, undoubtedly, an eccentric inventor. Such a description neither perfectly fits Harcourt the chemist, nor the highly imaginative and mathematical Dodgson. Harcourt, however, was sometimes absent-minded, as Dodgson recorded;

Harcourt had asked me to come and dine with him and Mrs H. I arrived at the hour fixed ($7\frac{1}{2}$), and had a very pleasant chat with Mrs H. till past 9! when Harcourt arrived, having forgotten all about it, and gone on in the laboratory.²

But it is in the chemical parallels between Harcourt and the White Knight that the temptation to draw an analogy is greatest. Harcourt's contribution to chemistry was unique in many ways, as we shall see. He recognised at a very early stage that what chemists had always neglected was the close observation of the actual course of chemical change, of the time factor involved in these changes. The key to chemical processes, for Harcourt, lay in establishing mechanical laws. The foundations for these ideas were laid at the very beginning of Harcourt's long career at Oxford, but he was to

1. The Ann. Alice, op.cit. ,307

2. Diaries, op.cit.

spend the subsequent fifty years perfecting his techniques. Forty-seven years were to pass between the first paper on the course of chemical change by Harcourt and Esson in the Proceedings of the Royal Society in 1865 and their last paper together in Philosophical Transactions of 1913.

It is difficult not to see a parody of the chemist labouring in the laboratory in Dodgson's witty lines on the exploits of the White Knight. Dodgson's characteristic play on words is illustrated here with the use of "course", which was also one of Harcourt's most frequently used chemical expressions:

"Now the cleverest thing of the sort that I ever did", he went on after a pause, "was inventing a new pudding during the meat course."

"In time to have it cooked for the next course?", said Alice. "Well, that was quick work, certainly."

"Well, not the next course", the Knight said in a slow thoughtful tone: "no, certainly not the next course."

"Then it would have to be the next day. I suppose you wouldn't have two pudding-courses in one dinner."

"Well, not the next day", the Knight repeated as before, "not the next day".

"In fact", he went on, holding his head down, and his voice getting lower and lower, "I don't believe that pudding ever was cooked. In fact I don't believe that pudding ever will be cooked. And it was a very clever pudding to invent."

"What did you mean it to be made of", Alice asked, hoping to cheer him up, for the poor Knight seemed quite low-spirited about it.

"It began with blotting paper", the Knight answered with a groan,

"That wouldn't be very nice, I'm afraid"

"Not very nice alone", he interrupted, quite eagerly, "but you've no idea what a difference it makes, mixing it with other things - such as gun-powder and sealing wax"

Harcourt and Dodgson remained close friends during their long careers at Oxford. Certainly, Dodgson's extensive diaries record many visits to Harcourt's ancestral home at Nuneham and to London together with his friend, whose company he obviously enjoyed. It might be thought strange that so few letters between Harcourt and Dodgson exist among the many that have survived. But as Professor Morton Cohen points out in his edition of Dodgson's letters¹, this attests to the closeness of their friendship rather than the opposite. In the days when no telephones existed, every piece of communication was by paper, and a great deal more was recorded for posterity than today, except when meetings were frequent.

Whether the White Knight was Dodgson himself, or a caricature of his chemist friend Harcourt, or, more likely,

1. In press. See also R.Lancelyn Green, The Diaries of Lewis Carrol, 2 Vols., Oxford, 1954.

a conglomeration of both and more besides, remains a fascinating conjecture. Harcourt was certainly there when the tales of Alice were conceptualised, and was present at the end, to witness Dodgson's will.

"Ever drifting down the stream, Linger in the golden gleam, Life, what is it but a dream?", wrote Dodgson of those halcyon days. The quality of Harcourt's superb chemical labours of fifty years has been appreciated by many a chemist since, and will be discussed in the next section, but, no doubt, it is the chemical exploits of Alice's White Knight which will continue to intrigue.

2.4.4 Experiments with Time

It may be merely a happy coincidence that we owe the quantified laws of mass action, first suggested by Berthollet, to two groups each of which comprised a teacher of chemistry and a mathematician. To Guldberg and Waage is usually attributed the first generalised expression relating quantity and velocity of reaction, as we have seen. But almost simultaneously, and it would appear quite independently, Harcourt and Esson were making similar discoveries. The premises on which the two groups embarked on their rate studies, however, are notably different. Whereas the two Norwegians were searching for elucidation of the laws of chemical affinity - and failed, Harcourt and Esson began their research far from any confines of affinity forces. From the very beginning, Harcourt's arguments centred around comprehension of the process of chemical change. Every change observed, Harcourt reasoned, whether chemical or physical, presents intrinsically two problems, the manner or course of the change and secondly, the results of the change.¹ The changes wrought by time, cosmic changes, seasonal changes, the succession of animal and vegetable species, form the basis of our major studies in the natural sciences. Observation of the course of chemical change, however, presented special problems. In order that the observations may be made accurately, the changes must

1. Chem. News, 1864, 10, 171-173.

necessarily proceed slowly, under conditions which are known at any instant; the changes occurring must also proceed sufficiently slowly for the amount of reacting substances to be measured. And the changes taking place should be simple rather than complex.

In 1867, some three years after the appearance of Harcourt and Esson's first paper on the rate of chemical change, the problems of such an ideal system still remained unresolved. Reporting in the Journal of the Chemical Society, Harcourt wrote,

I am acquainted with only two observations of the course of gradual chemical changes, similar to those which I have attempted to make. In the course of their photo-chemical researches, Professors Bunsen and Roscoe examined the action of bromine upon tartaric acid in a dilute aqueous solution in order to discover whether an acceleration occurs in the early stages of the action. They appear to have established the fact that such an acceleration does occur, and compare with it the similar phenomenon of chemical induction. More recently, an elaborate investigation into the synthesis of compound ethers has been published by Mr. Berthelot.¹

Among the chemical systems which Harcourt initially

1. J. Chem. Soc., 1867, 20, 461.

considered in his rate studies were heterogeneous phases furnished by the precipitation of a barium and a calcium salt from their solutions upon the addition of a sulphate; the reduction of a chromate by a sulphite and by an oxalate was also considered. The first reaction occupied no appreciable time - but these results were not investigated fully, for Harcourt reported that the actual time of reaction could have been controlled better in a more dilute solution and at a lower temperature.¹ In the second case, with an oxalate as reducing agent, though the final result of the change was the same, the action took a long time to be accomplished and offered a more practical system for study.

In order to establish an exact experimental method for measuring the rate of chemical change, Harcourt had devised the following experiment:

The solution of ammonium nitrate, heated to a temperature of about 80°C in a flask provided with a gas delivery tube, gives off a quantity of nitrogen, which may be collected over the pneumatic trough. By keeping the temperature constant, and collecting the gas evolved during successive equal intervals of time in similar cylinders, it is possible at once to show the regular diminution on the volume of gas which is caused by the constant diminution of the quantity of

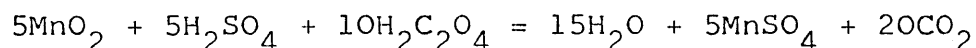
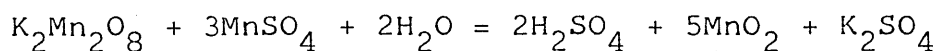
1. Chem. News, 1868, 18, 14.

salt in solution. By making the experiment and measuring the quantities of gas with accuracy, it would be possible to discover the relation between the amount of change going on at any moment and the amount of salt in solution, and also, by making the experiment at different temperatures, to discover how the temperature of the solution affects the rate at which the action takes place.¹

(Many years later, Harcourt was to devise a method for observing the rate of action of a liquid upon a solid. The method employed a motor to drive the liquid to-and-fro in the arms of a U-tube, using a form of hot air engine, also invented by Harcourt. The work was reported in the American Association Proceedings of 1897, but Harcourt's later work does not appear to have utilised the apparatus in further investigations.²)

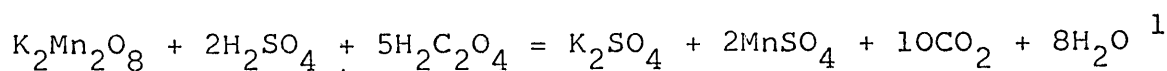
But the system which Harcourt eventually selected for study was the action between potassium permanganate solution in dilute sulphuric acid and a solution containing manganous sulphate and excess of oxalic acid. For this system he gave the following sequence of reactions:³

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1. Chem. News, 1868, 18, 14.
 2. Am. Ass. Proc., 1897, 153.
 3. Chem. News, 1864, 10, 171-173.



The reaction occurs at ordinary temperatures and it was thus possible to keep the temperature of the solution constant during the whole period of experimentation. Harcourt's reasons for choosing this system had been carefully considered. The reaction took place in a convenient interval of time and could be started and terminated at a given moment. The reagents, too, were available in a pure state and, as liquids, were convenient to handle. By considerable numbers of trial and error, Harcourt determined that by carefully controlling the experimental conditions, the amount of change observed in successive experiments always remained the same. This change was dependent only upon the amount of each of the four substances named above, upon the dilution and temperature of the solution and upon the time during which the substances were left in contact.

Despite these seemingly ideal conditions, Harcourt very early on recognised that the reaction was not a simple one-step reaction but took place in different stages, as we shall see. The principal complication arose from a secondary reaction which took place between permanganic acid and the manganous salt formed by it's reduction. It was necessary to include manganous sulphate among the reagents, the effect of whose variation was being investigated. The overall reaction they gave as:



1. Proc. Roy. Soc., 1865, 14, 470-474.

In particular, the effect of varying the temperature was not investigated at this time, owing to the discovery of the complex nature of the chemical change. This important aspect of their chemical studies had to wait until 1912 before elucidation, in what was to be Harcourt and Esson's last major publication.

The experimental method adopted by Harcourt was as follows:

Measured quantities of the standard solutions of oxalic acid, sulphuric acid and manganous sulphate were mixed with a measured quantity of water and the whole brought to a temperature of 16°C . A measured quantity of a standard solution of potassium permanganate was added and the time of the addition noted. Throughout the course of the reaction, the temperature, observed by a thermometer inserted in the solution, was kept rigorously constant. When the required interval had elapsed, an excess of potassium iodide was added, and the liberated iodine, which indicates the amount of permanganic acid present, was estimated by titration with a standard solution of sodium (sodic) hyposulphite.¹

Having selected the chemical system which he considered best suited to his purpose and ascertained a

1. Proc. Roy. Soc., 1865, 14, 471.

successful technique of experimental analysis, Harcourt proceeded to investigate the problem of chemical change. At the outset of these experiments it is doubtful if he could have foreseen the complications which were to arise. His first memoir on the permanganate/oxalic acid reactions, in what was to be but the beginning of a long series of experiments, was published in the Chemical News of 1864, the paper, entitled simply 'On the Rate of Chemical Change', was short and his method of approach equally direct. In this, he reported carrying out a series of experiments in which all the conditions previously considered were maintained constant apart from one, which was varied increasingly.¹ His objective was to:

determine what function of each of these variable quantities the chemical change is, and so to obtain a true expression of the reaction.²

At this stage he had already been joined by Esson, for in the same paper, which was read before the British Association Bath Meeting of 1864, he wrote:

... a large number of experiments already described have been performed by my friend, Mr. Esson, Fellow of Merton College, Oxford, who has charged me with the office of bringing before the Section some account of our joint work.³

1. Chem. News, 1864, 10, 171-173

2. ibid., 172

3. B.A. Report, 1864, 2, 30.

Harcourt observed that of all the factors which affected chemical change, the time factor was the most flexible. It was a major factor on which they were to base this and other sequences of experiments. He wrote:

I made, for example, a series of experiments, in all of which I took the same quantities of permanganic acid, oxalic acid, sulphate of manganese, and water, maintaining always a temperature of 16°C and allowing each experiment to proceed for exactly five minutes ... when five minutes from the moment of mixing had expired, the action was stopped and the amount of permanganate still remaining determined.¹

The experiments yielded a series of data, which from its perfectly regular decrease, made Harcourt and Esson realise that they were observing a law of chemical reaction, which had yet to be formulated. A graphical plot of their results, showing the smooth hyperbolic shaped transition between the reactants and the products with time, was insufficiently conclusive. But this focused their attention onto another series of experiments from which they derived some quite unexpected hypotheses.

The series of experiments which appeared most interesting was that in which, all other conditions being kept constant, the

1. Chem. News, 1864, 10, 172.

time during which the experiment lasted was varied.¹

The experimental procedure, they described as follows:

The solution containing all the substances except the permanganate was brought to the required temperature, and the permanganate added from a pipette exactly at the beat of a seconds' pendulum. When the time had expired, the temperature of the solution having been kept rigidly constant throughout, a solution of iodide of potassium was added, again at the beat of a clock....The addition of iodide of potassium stops the action. The remaining permanganate is at once reduced, and liberates thereby an equivalent of iodine which can be determined at leisure in the usual way. Of such series of experiments I have made a great number.²

Such a series of experiments yielded a curve which was similar to that representing the effect of varying the amount of sulphuric acid, indicating that their first curve was, in fact, a general representation of chemical progress with time. Since the curve approached the x-axis asymptotically, the reaction, theoretically, never ends:

The result at which we believe ourselves to have arrived is, that the numbers representing the quantities remaining after equal intervals

1. Chem. News, 1864, 10, 172.

2. ibid., 173

of time, are in geometrical progression, and the curve consequently a logarithmic curve.¹

At the end of this particular analysis, however, their objective had not been achieved; the results were still far too generalised. But though unable to deduce the equation fitting the curve at the time, Harcourt and Esson developed a theory suggestive of later reaction mechanism; consider, they said, that the dissolved binoxide (i.e. MnO_2) exists in the fluid in the form of minute spheres upon whose unit of surface is performed a constant action. The total action thus, at any moment, varies with the surface exposed, and diminishes continually as the spheres, shell after shell, melt away.

As an alternative, they proposed that if the binoxide of manganese is replaced as it disappears, so that the quantity present is always the same, then the chemical change will proceed at a uniform rate - since no condition alters, a certain fraction of the whole amount disappearing in a unit of time. But the quantity of one substance (the solution) is present in such excess compared to the binoxide, that their relative proportions remain constant, even though the binoxide is not replenished. In concluding their analysis, they made the intriguing remark:

the amount which changes during a moment

1. Chem. News, 1864, 10, 173.

of time is directly proportional to the total amount existing in solution at that time; or, if we regard the binoxide as doing work - oxidising oxalic acid - then the statement is that the amount of work done is directly proportional to the amount of substance which at any time is there to do it.¹

The idea that a chemical substance was doing work appears as a startling conjecture, the year being 1864 and a time when some chemists were still deeply engrossed in the Atomic Debate. This reference to work being done no doubt stems from the direct analogy to physical systems which remained close in the minds of the two men. In subsequent researches, the idea of work is replaced by potential, equally startling and again physical in origin. Harcourt was reasonably confident that their approach was close to the deduction of a general rate law which would pass inductively "to a generalisation covering those cases of chemical change which take place with an immeasurable velocity," for whatever reasons. This depended upon finding a chemical system which permitted analysis, was sufficiently slow to enable the speed to be measured and was capable of being started and terminated at will.

Just as by the use of the pendulum or of Atwoods' machine we may prove experimentally

1. Chem. News, 1864, 10, 173.

the laws of falling bodies, when in the common case of bodies falling freely the velocity with which they move is too great for measurement.¹

In their next researches, Harcourt and Esson had found a satisfactory system which met these criteria, and stated for the first time, the law relating mass of substance and its rate of reaction.

Two years later, in the Philosophical Transactions of 1866, they restated the problem with increasing confidence, based on their previous findings:

When any substances are brought together under circumstances under which they act chemically one upon another, a change takes place which consists in the disappearance of a part of the original substances and the appearance of an equal weight of other substances in their place. This change continues, if the circumstances remain the same, until the whole of one of the substances taking part in it has disappeared. Its total amount is therefore ultimately determined by the amount of that substance which was originally present in the smallest proportional quantity. The attainment of this limit, as will be shown, requires theoretically an infinite time,

1. Chem. News, 1864, 10, 173; B.A. Report, 1864, 2 29-31.

but the velocity of chemical change is so great that the practical limit of an inappreciable residue is in most cases speedily reached.¹

Having thus clearly enunciated the nature of the chemical problem, they go on to say:

Owing perhaps to this fact, chemists have been led to bestow their chief attention upon the result, and not upon the course of these changes. Occupied in investigating the relation between the reagents and the ultimate products of a reaction, and studying the chemical and physical properties of the thousand different substances thus produced, they are accustomed to regard the various conditions under which every chemical change takes place, and by which its amount is determined, chiefly as means to an end, as points to be attended to in a receipt for preparing one substance from another.²

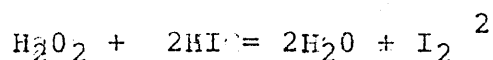
Harcourt and Esson's objective was to quantify the laws relating the amount of substance taking part in chemical reactions to the physical factors controlling the process, the temperature, and the time during which the substances are reacting. Many of the problems yet to be overcome, they discovered, were of a purely practical nature:

1. Phil. Trans., 1866, 156, 193.

2. Phil. Trans., 156, 193, (1866).

the number of cases in which the investigations of these is practicable is extremely limited. In the first place, it must be possible both to start and terminate the reaction abruptly at a given moment. In the next, either some product or some residue of the action must be a substance for whose estimation exact and ready methods are known, so that the amount of change may be quantitatively determined. Lastly, all the conditions of the reaction must be measurable¹, or at least definable.....

The reaction which best fulfilled these conditions, Harcourt and Esson considered to be that of 'hydric peroxide and hydric iodide' in acidified solution;



The experimental procedures for the investigation are set out in their paper in the minutest detail together with the difficulties of quantative measurements:^{ti/}

since..... the addition and mixing are far from being instantaneous an experiment was not made to date from this point,

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1. Phil. Trans, 1866 156, 193-4
 2. The sequence of changes for this reaction is a standard, used in volumetric analysis today. The peroxide (present in excess) oxidises the iodide to free iodine. Thiosulphate will instantly remove the iodine and, with starch as indicator, the familiar starch-iodine colour appears when all the ^{thio/}sulphate has been used up.

but from the moment of the appearance of the blue colour. In order that the second at which this change occurred might be accurately noted, the cylinder was placed on a sheet of white paper in a good light, and opposite to it was stationed a clock beating seconds.¹

The temperature of the reaction was controlled by means of an iron plate, heated at one end by a lamp.

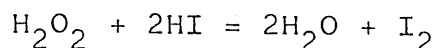
The observations were made by looking down upon the column of fluid and watching the appearance of the disk forming its upper surface, listening at the same time to the beat of the clock and counting the seconds. So suddenly does the blue shade pass over the clear and brightly illuminated disk, that a practised observer can generally feel sure as to the second in which the change begins. And when the reaction is proceeding very rapidly, it would often be possible to subdivide the second.²

As soon as the observation had been made, a drop of hyposulphite was added which restored the liquid to its original colourless condition. The time that elapses between two successive appearances of the blue colour becomes continually greater as the amount of peroxide in the solution diminishes, and finally the last measure of hyposulphite requires more iodine for its

1. Phil. Trans., 1867, (157), 120.

2. Phil. Trans., ibid.

conversion than the residual peroxide can furnish, and the blue colour does not return. The amount of peroxide may then be determined by means of a 'back-titration' with a standard solution of permanganate. Harcourt and Esson considered that the decrease of the peroxide was a measure of the amount of chemical change. Each time that the operation represented by



is performed, a molecule of peroxide disappears. As the experiment proceeds, the observed time intervals represent the successive portion of chemical change taking place. In this way, they were able to achieve their goal, namely to start and terminate the reaction abruptly at a given instant with the ability to determine the quantitative values of the substances taking part in the reaction. As the quantity of peroxide diminishes, the amount of chemical change in a unit of time diminishes, or in other words, the time required for the accomplishment of a unit of chemical change increases.

The difficulties experienced in rigorously controlling the temperature, they discovered, were to result in discrepancies. Though, generally, the rate was observed to increase with temperature, the overall effect was complex, a phenomenon which they later investigated in detail. At the end of their paper, Harcourt and Esson concluded;

.... and whether the portion of change require for its accomplishment intervals of one or two minutes, or intervals of half an hour or an

hour, this reaction still confirms to the law that the amount of change is at each moment proportional to the amount of changing substance.¹

Following the publications of their work in the Philosophical Transactions of 1866, 1867, Harcourt gave a further detailed account of the experimental techniques entailed in the reactions they had recently completed. This account, which appeared in the Journal of the Chemical Society, amounted to thirty pages.² Among the precautions taken during the reaction sequence were corrections for the small amount of reactant adhering to the pipette after the main body of fluid had been transferred to the reaction vessel.³ The degree of precision and systematic methods used throughout their work is indeed difficult, if not impossible, to describe accurately, without resorting to their own description.

It would also be difficult to try and imagine how their work was received by the chemical community of that time. It seems not unreasonable to imagine that the greater part of the work could not be easily understood by the majority of chemists, particularly the detailed mathematical analysis which followed each experimental report. Indeed, many of their formulations were

1. Phil. Trans., 1867, 157, 127-8.

2. J. Chem. Soc., 1867, 20, 460-492.

3. ibid., 477-478.

perhaps complicated even for their mathematical contemporaries.¹ It is generally accepted that the merit of their work was not recognised until the laws of chemical kinetics had been fully established on the basis of other considerations and the work of many other researchers, among whom ^{were} numbered many of his own students.

Whether lack of comprehension by their contemporaries was the motive, Harcourt re-summarised the major conclusions of their work at the weekly evening meeting of the R.I. in February, 1868:-

The following propositions embody the principal conclusions to which the examination of these cases of gradual chemical change has led:-

1. The rate at which a chemical change proceeds is constant under constant conditions, and is independent of the time that has elapsed since the change commenced.
2. When any substance is undergoing a chemical change, of which no condition varies, excepting the diminution of the changing substance, the amount of change occurring at any moment is directly proportional to the quantity of the substance.
3. When two or more substances act one upon another, the amount of action at any moment is directly proportional to the quantity of each of the substances.

1. See Obituary, William Esson: Proc. R. Soc. 1917, (93) liv-lvii.

4. When the rate of any chemical change is affected by the presence of a substance, which itself takes no part in the change, the acceleration or retardation produced is directly proportional to the quantity of the substance.
5. The relation between the rate of a chemical change occurring in solution, and the temperature of the solution, is such, that for every additional degree the number expressing the rate is to be multiplied by a constant quantity.¹

More interesting than the experimental procedures, for the purposes of this thesis, is the theoretical and mathematical interpretation given throughout their published work. Totally void of the 'chemical affinity' theories of the day, their papers entitled 'On the laws of Connection between the Conditions of a Chemical Change and its Amount'² sought for a physical analogy in which time was the essential factor:

In each set of experiments we commence with a system which contains elements capable of under-going a certain quantity of change. We may express this by saying that there exists at starting a certain amount of potential change. As time elapses this potential change gradually becomes actual. From this point of view the change occurring in the system is analogous to

1. Proc. R.I. of Gt. Brit., 1868, 304-308.

2. Phil. Trans., 1866, 156, 193: 1867, 157, 117

the motion of a heavy body falling freely, which at the commencement of its motion has a certain amount of potential energy capable of being transformed into actual energy. As the body falls the potential energy gradually becomes actual. Each experiment supplies data for the determination of the following quantities:-

- (1) the initial potential change
- (2) the final potential change
- (3) the actual change
- (4) the time during which the actual change has occurred.¹

The analogy between the two systems, the chemical and physical, is carried to considerable lengths so that the differential equation at the end appears perfectly appropriate:

The relation existing between these quantities has been found to be of such a nature that the ratio of the initial and final potential changes in a given system depends only upon the time of the actual change, so that if this time is constant the ratio is constant; and since the actual change is simply the difference between the initial and final potential changes, it follows that for equal intervals of time the actual change is proportional to the initial potential change.²

1. Phil. Trans., 1867, 157, 128-9.

2. ibid., 129 .

Wilhelmy had already introduced the form of differential notation for rate of chemical change, but the extent of its acceptance into realms of chemical analysis around 1860 is doubtful. In physics, of course, the rate of progression (v) of a body can be represented simply by $v = ds/dt$, with usual notation, and assuming that the time change, dt , is so small that the rate of change has not altered appreciably. Thus Harcourt and Esson had proceeded to analyse chemical systems in terms which were familiar, mechanically. If, they thought, they could construct a system in which the potential change remained constant, clearly the actual change would proceed at a uniform rate. However, in the chemical system, the potential change varies so that no direct observation of the uniform rate of change is possible. Indirectly, however, they reasoned:

Suppose the time of actual change to be so small that its rate may be considered uniform during that time, the actual change will be so small that the initial and final potential changes may be considered to be equal; in other words, the potential change will be constant. The ratio of the small actual change to the time of its occurrence will thus represent the uniform rate of actual change when the potential change remains constant. The equation which connects the initial and final potential changes y , y' with the time of actual change has been found to be

$$y/y' = e^{a(t' - t)}$$

whence we obtain

$$-dy/dt = ay$$

Now $-dy$ is the actual change which occurs during the time dt ,...it follows therefore that in a given system, in which there exists a constant quantity of potential change y , the uniform rate of actual change is ay . Or since a is constant for the given system, the rate of actual change is proportional to the potential change. If the unit of time is one minute, a represents the fraction of the potential change which is converted into actual change in one minute.¹

The reaction between hydrogen peroxide and hydrogen iodide was also to be the subject of their major publication, the Bakerian Lecture of 1895. This comprehensive work, almost eighty pages long, summarised the experimental results of their thirty years labour.² In addition, they had carried out variations on the previous work by substituting salts with the same metal or acid radicle, but the results were not notably revealing.³

The greatest advance made in this publication was the detailed study of the result of the variation of temperature, a condition which had previously caused them considerable problems. At the time, they had considered the complex nature of the reaction too difficult to attempt a detailed temperature study. The variation of reaction rate with temperature was to be the subject of another,

1. Phil. Trans., 1867, 157, 129.

2. Phil. Trans., 1895, 186a, 817-895.

3. ibid., 847.

separate publication, which they made together in 1912, incidentally their last. The importance of this contribution will be discussed separately.

But in the Bakerian Lecture, they gave for the first time the expression,

$$\frac{\alpha_t}{\alpha_0} = \frac{(272.6 + t)^m}{(272.6)^m}$$

where α_t , α_0 are measures of chemical change at temperatures t , $^{\circ}\text{C}.$, and m is a constant depending upon the experiment.¹ The derivation of this expression, which arose empirically from experimental results, was largely the work of William Esson as many sources, including Harcourt himself, testify.² The equation implied that at a temperature $t = -272.6$, no chemical change will take place. This temperature they recognised as being almost identical with absolute zero, $-273^{\circ}\text{C}.$ Harcourt and Esson hence concluded that at this point molecules would be at rest, and no chemical change would be possible. The zero of chemical change coincides with the zero of absolute temperature. For Harcourt and Esson it was a fitting conclusion to a lifetime of work involving the study of gradual chemical change.

1. Phil. Trans., 1895, (186A), 860

2. See obit. (op. cit.) and R.S. letter, and later section on temperature/rate.

The two mammoth publications of 1895 and 1912, were worthy summaries of almost half a century of shared labour, unusual for its chemical and mathematical rigour. In order to give an indication of the depth of analysis, the Appendix to their publication of 1866 is given in full. The rate expressions derived by Esson cover, as we can now appreciate, first and second order reactions as well as special cases of more complicated nature. They showed, in the process, that theoretically, chemical reactions could only approach completion at infinite time. In this they had been anticipated by Wilhelmy. But in the depth of analysis to which they had subjected the whole study of the course of chemical reactions, they were undoubtedly pioneers. Harcourt and Esson's work firmly established the vital concept of time into the very ancient phenomenon of chemical change.

APPENDIX

*containing a Theoretical Discussion of some cases of Chemical Change.**By WILLIAM ESSON, M.A., Fellow of Merton College, Oxford*

The most simple case of chemical change occurs in a system in which a single substance is undergoing change in presence of a constant quantity of other substances, and at a constant temperature. A practical constancy of the other substances is obtained by having them present in large excess; for any change produced in their amount by reason of the change of the single substance is infinitesimal in comparison with their original amount, and its effect on the system may therefore be neglected.

By a "system" is meant a unit of volume in which given quantities of substances are present; these quantities are called "elements of the system;" "a system in which a single substance is undergoing change," is a system in which the variation of the other substances does not affect the change of the single substance.

It has been ascertained by experiment that the residue y of the substance undergoing change in a system of this kind, is connected with the time x during which the change has been proceeding, by the following equation,

$$y = ae^{-ax}, \quad (1)$$

a being the quantity of the substance in the system at the commencement of the change, and a a constant, the meaning of which may be thus determined; differentiating (1) and eliminating x , we have

$$\frac{dy}{dx} = -ay. \quad (2)$$

Now $-\frac{dy}{dx}$ is the amount of substance which disappears in a unit of time at the time x , when y is the quantity of substance present in the system, and the equation (2) expresses the law that "the amount of change in a unit of time is directly proportional to the quantity of substance;" following the analogy of the motion of a material particle, we may call $\frac{dy}{dx}$ the rate or velocity of chemical

change, and the law may be thus stated:—"The velocity of chemical change is directly proportional to the quantity of substance undergoing change."

The constant a expresses the fraction of the substance which is changed in a unit of time; this fraction depends upon the other elements of the system, and upon its physical conditions, such as temperature, density, etc. By varying each of these conditions in succession, it is possible to determine a as a function of them, and to predict the progress of the chemical change of a single substance, from its commencement to its completion, under any assignable conditions.

Let us first take the case in which the chemical change consists of the reaction of two substances, neither of which is present in the system in great excess. In the discussion of this case we shall assume the general truth of the law of variation of the rate of chemical action, which has been derived from experiments in which the constancy of all the elements but one has been secured by taking them in excess. In fact we shall assume that the truth of the law depends only upon the constancy of the elements, and not upon their excess. Since, then, the velocity of change of each

substance is proportional to its quantity when the quantity of the other is constant, it follows that the velocity of change is proportional to the product of the quantities when both vary. Let a, b be the number of equivalents of the substances present in the system at the commencement of the reaction, z the number of equivalents of each which has disappeared during a time x , then $a-z, b-z$ are the number of equivalents remaining at the end of that time; hence

$$\frac{dz}{dx} = n(a-z)(b-z), \quad (3)$$

the solution of which is

$$\log \left(1 - \frac{z}{a}\right) - \log \left(1 - \frac{z}{b}\right) = n(a-b)x, \quad (4)$$

an equation for determining the amount of chemical change, in this case, after the lapse of a given time.

When the substances are originally present in equivalent quantities, $a = b$, and (3) becomes

$$\frac{dz}{dx} = n(a-z)^2, \quad (5)$$

the solution of which is

$$z = a \frac{nax}{nax + 1}. \quad (6)$$

The equation connecting the residue y with the time is in this case

$$y = \frac{a}{nax + 1}; \quad (7)$$

and if at the commencement of the reaction the substances had been present in infinitely large quantities,

$$y = \frac{1}{nx}. \quad (8)$$

The curve (6), which expresses the reaction of two substances originally present in equivalent quantities, is a rectangular hyperbola, and when the original quantities are infinite, the residue varies inversely as the time.

Let us suppose that at the commencement of the reaction there are present a equivalents of a substance A, which during the course of the reaction is gradually changed into an equivalent quantity of a substance B, and that B reacts with a substance C of which a equivalents are originally present; also let u be the number of equivalents of A which remain after an interval x , and v the number of equivalents of B which remain after the same interval; then, since the velocity of diminution of u is proportional to its quantity, and the velocity of diminution of v proportional to the product of its quantity into the quantity of c , and the velocity of increase of v equal to the velocity of diminution of u , we have the following equations,

$$\frac{du}{dx} = -\beta u, \quad (9)$$

$$\frac{dv}{dx} = -\alpha v(u+v) + \beta u. \quad (10)$$

The solution of (9) is

$$u = ae^{-\beta x}; \quad (11)$$

so that if the residue of u could be measured separately from that of v , the rate of change of u into v could be determined, but in the actual experiments u and v are determined together, and the relation between the total residue $y(=u+v)$ and the duration of the reaction x is consequently very complex.

Adding (9) and (10), we have,

$$\frac{dy}{dx} + \alpha y = 0; \quad (12)$$

substituting for dx from (9), and for v its value $y-u$, we obtain the equation

$$\frac{dy}{y^2 du} + \frac{\alpha}{\beta y} - \frac{\alpha}{\beta u} = 0, \quad (13)$$

the solution of which is

$$\frac{\alpha}{\beta} e^{\frac{\alpha}{\beta} u} \left\{ c - \log u + \frac{\alpha}{\beta} u - \frac{1}{1.2} \left(\frac{\alpha}{\beta} u \right)^2 + \dots \right\} y = 1. \quad (14)$$

If we replace for u its value $ae^{-\beta x}$, we obtain an equation connecting the residue y with the time x .

The next case to be considered is that of a system in which there are two substances undergoing change in presence of a large excess of the other elements of the system. If both substances are present in the system from the commencement of the change and are independent of each other, the velocity of diminution of each is proportional to its quantity, and their residues accord with the simple law $y = ae^{-\alpha x}$; and if both these residues are measured together, the equation of the reaction is

$$y = a_1 e^{-\alpha_1 x} + a_2 e^{-\alpha_2 x}, \quad (17)$$

a_1, a_2 being the quantities of the substances originally introduced into the system, and α_1, α_2 the fractions of them which disappear in a unit of time.

If, however, the substances are not independent, but are such that one of them is gradually formed from the other, we have a different system of equations to represent the reaction.

Let u, v be the residues of the substances after an interval x , y ($=u+v$) being the total residue actually measured at that time. Let the initial values of u and v be $u=a, v=0$; let αu be the rate of diminution of u due to its reaction with one of the other elements of the system, and βu its rate of diminution due to its reaction with another of the elements of the system, by means of which v is formed, and let γv be the rate of diminution of v , then

$$\frac{du}{dx} = -(\alpha + \beta)u, \quad (18)$$

$$\text{whence} \quad \frac{dv}{dx} = \beta u - \gamma v, \quad (19)$$

$$u = ae^{-(\alpha + \beta)x}, \quad (20)$$

$$v = \frac{\alpha\beta}{\alpha + \beta - \gamma} \{e^{-\gamma x} - e^{-(\alpha + \beta)x}\}, \quad (21)$$

$$y = \frac{\alpha}{\alpha + \beta - \gamma} \{\beta e^{-\gamma x} + (\alpha - \gamma)e^{-(\alpha + \beta)x}\}. \quad (22)$$

There are several particular cases of these equations which require to be considered separately.

(1) $\beta=0$. Fraction of v formed $=0$.

In this case the system of equations reduce to

$$u = ae^{-ax},$$

$$v = 0,$$

$$y = ae^{-ax}.$$

(2) $\gamma > a$. Fraction of v decomposed in a unit of time, greater than the fraction of u decomposed in a unit of time.

In this case the last equation of the system is of the form

$$y = a_1e^{-a_1x} - a_2e^{-a_2x}.$$

(3) $\gamma = a$. The fraction of v decomposed in a unit of time equal to the fraction of u decomposed in a unit of time.

In this case the last equation of the system reduces to the form

$$y = ae^{-ax}.$$

(4) $\gamma < a$. The fraction of v decomposed in a unit of time greater than the fraction of u decomposed in a unit of time.

In this case the last equation of the system is of the form

$$y = a_1e^{-a_1x} + a_2e^{-a_2x}.$$

It is thus possible to have all these four cases in succession in a set of experiments in which only one condition is progressively varied, provided that the variation of γ and a is such that γ is at first greater than a , but increases in a less ratio than a . Several attempts have been made to calculate equations of the form $y = a_1e^{-a_1x} \pm a_2e^{-a_2x}$ which should give the experimental numbers within the errors of experiment, and at the same time yield values of the fractions a, β, γ from which the law of their variation with a variable quantity of sulphuric acid could be discovered. The number and exactness of the experimental results are, however, not sufficient to enable us to extract from the complicated equation

$$y = \frac{a}{a+\beta-\gamma} \{ \beta e^{-\gamma x} + (a-\gamma) e^{-(a+\beta x)} \}$$

trustworthy values of α , β , γ , and this inexactness precludes the possibility of investigating the law of their variation when the conditions of the experiment are varied. What we can state with certainty is, that the numbers are all satisfied by equations of the forms

$$y = a_1 e^{-\alpha_1 x} - a_2 e^{-\alpha_2 x},$$

$$y = a e^{-\alpha x},$$

$$y = a_1 e^{-\alpha_1 x} + a_2 e^{-\alpha_2 x},$$

and that successive sets of numbers, obtained by varying one condition progressively, are satisfied by these successive forms of equations. These forms, and the order of their succession, are accounted for by a hypothesis for which there is considerable experimental evidence, and it is thus highly probable that the results arrived at in the above discussion give a true account of the progress of the reaction.

The law of variation of α , β , γ with the conditions of the system will probably be detected when the case in which β , γ both vanish for all conditions of the system, has been fully discussed.

A complete investigation of this case is reserved for a future communication.

2.4.5 The Influence and Application of Harcourt and Esson's Work

Harcourt and Esson's work was exceptional in several ways. First, the precision and systematic method of their research, both experimental and theoretical, was perfected to a degree of accuracy which, even today, remains largely unsurpassed.¹ Secondly, the complexity of their chosen chemical system and subsequent results compelled them to continue their studies over a period which spanned almost 50 years. The rate studies on chemical systems initiated by them pioneered a tradition of physical chemistry at Oxford which shows a continuous influence on the development of chemistry. Their work appeared at a time when many scientists, including Harcourt himself, considered British science to be in a state of unhealthy decline. It may be useful here to summarise the major results of Harcourt and Esson's work.

(a) In their work on the reaction between hydrogen peroxide and iodide, they established a general law of chemistry: when any substance is undergoing chemical change, of which no condition varies except the diminution of the changing substance, the amount of change occurring at any instant is directly proportional to the quantity of substance.² This is an expression of the law of Mass Action.

1 The two major reactions investigated by Harcourt and Esson involving iodide/peroxide and permanganate/oxalate, are common analytical exercises carried out by present generations of chemistry students.

2 J. Chem. Soc., 1867, 20, 460-492.

(b) The representation of the course of chemical reaction by logarithmic curves. Harcourt and Esson established that, assuming their law of proportionality holds good, the quantity of reacting substance at the end of a series of reaction times taken in arithmetical progression will be in geometrical progression - and could be represented by a logarithmic curve.

(c) Factors affecting chemical change. Harcourt established that various interdependent factors were responsible for the overall reaction rate; apart from the quantity of actual reacting substance, the amount of change was related to the time during which the reaction took place, the volume of the solution, and the temperature. For all these factors, Esson was able to establish mathematical expressions of varying complexities.

(d) As a corollary to their work on temperature, Harcourt reckoned that, for every 10° C temperature rise, the rate was approximately doubled.

(e) Esson deduced that at the absolute zero of temperature, not only do gases exert no pressure, their molecules having ceased to move, but atoms also cease to move and chemical change is no longer possible.

(f) The homogeneous system first chosen for study by Harcourt and Esson, that of permanganate and oxalic acid, was a particularly complex one, as we have noted. It was to lead to the idea that chemical reactions often occurred in more than one stage, but stages which were consecutive. The rate of chemical change was complicated by the phenomena of auto-catalysis as the result of a two-stage reaction, which

they were able to establish.

In the years following publication of Harcourt and Esson's work, a number of papers appeared which were based directly on their concept of the rate of chemical change.¹ One of the most comprehensive studies to utilize the laws of chemical change, as established by Harcourt and Esson, was a discussion by Cornelius O'Sullivan and Frederick Thompson, on the enzyme invertase. This appeared in the Journal of Chemical Society in 1890.² At that time, little was known about the nature of enzymes as a whole and even less was understood about their chemical constitution.³ O'Sullivan and Thompson hoped to determine whether reactions involving enzymes - or 'unorganised ferments', so called because they possessed a life function without life - could be distinguished from ordinary chemical reaction. Their work established that the course of an enzyme-catalysed reaction is kinetically indistinguishable from that of any other catalytic reaction. This discovery marks an important advance in the understanding of the chemistry of enzymes, and of biological chemistry in general.⁴

1 See for example: M.M. Pattison-Muir; 'Contributions from the Laboratory of Gonville and Caius College, Cambridge'; J.Chem.Soc.; 1879, 35, 311; 1880, 424.

E.J. Mills; Phil.Mag., 1872, 4, 48,241; ibid, 1876, 5, 1,1.

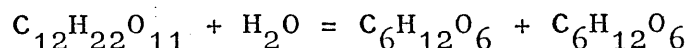
2 C. O'Sullivan, F.W. Thompson; J.Chem.Soc., 1890, 57, 834-928. Cornelius O'Sullivan FRS, 1841-1907. Chemist and later head brewer of Bass, Ratcliff and Gretton Ltd. in Burton-on-Trent. There does not appear to be an obituary of O'Sullivan in the Royal Society Journals.

3 The first enzyme, diastase, was isolated by Payen and Persoz in 1832; Ann.Chim.Phys., 1833, 2, 53, 73.

4 See S. Arrhenius, Quantitative Laws in Biological Chemistry, London, 1915.

O'Sullivan and Thompson initially chose invertase because it was available in large quantities. Subsequently, they found that the experimental results could be followed with relative ease and precision by means of polarimetry. Ten years prior to O'Sullivan's work, it had been established by Kjeldahl, that in the action of invertase on cane-sugar, the rate of transformation was proportional to the time until 40 per cent of the sugar was inverted.¹ The amount of inversion was independent of the quantity of invertase present, as in many catalytic reactions, but the time of the reaction did not follow the course of catalytic changes. The enzyme was known to be capable of inverting 750 times its own weight of sugar in 48 hours.²

Invertase converts cane-sugar to dextrose and laevulose (that is D(+) glucose and D(-) fructose) in the cold, the only known enzyme to do so:



The experimental procedure for carrying out the inversion is straightforward - for instance the reaction could be stopped at any time by the addition of excess alkali, either potassium or sodium hydroxide. The reaction mixture is stable and, theoretically, could be examined at leisure. O'Sullivan and Thompson discovered however, that it was necessary to wait 15 minutes after the reaction was complete before examining the results. Their earlier results, in which this time lapse had not been allowed, showed discrepancies which disappeared when the time factor was

1 O'Sullivan and Thompson, op.cit., 837.

2 ibid., 838.

accounted for.¹ The degree of inversion after specific time intervals was followed by means of a polarimeter.

Following closely the results outlined by Harcourt and Esson in their paper of 1867, O'Sullivan and Thompson analysed, very thoroughly, the inversion of cane sugar by invertase under the headings:

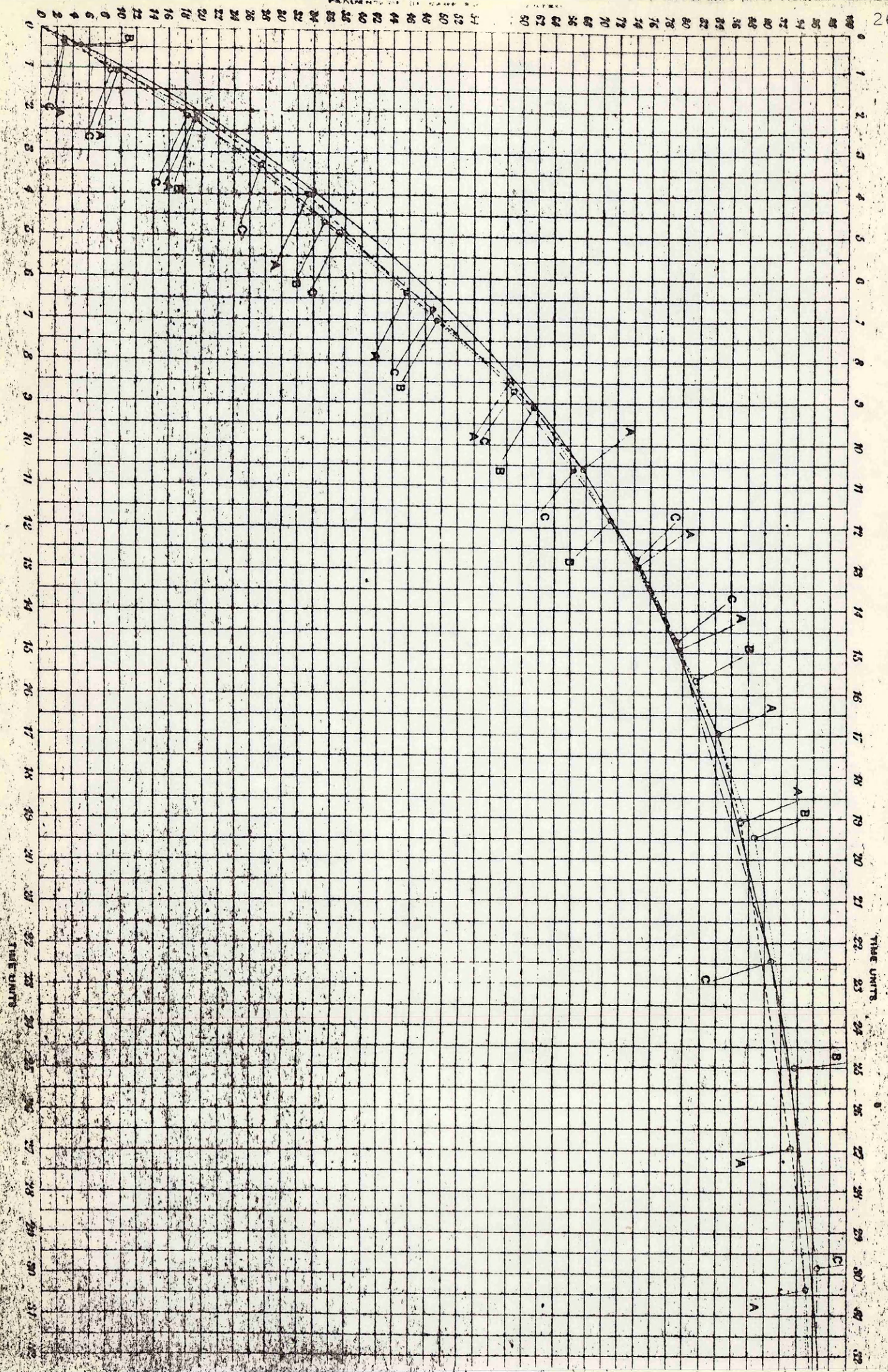
(a) The rapidity of Reaction

That the action of invertase was much faster at the beginning of a reaction than at the end was well known. O'Sullivan and Thompson first established a set of reaction curves, for 3 carefully conducted inversion experiments by plotting the percentage of sucrose inverted against time. (Labelled A, B, and C in their graph). They compared this to a theoretical curve, based on Harcourt's law of chemical change (shown as a continuous line). They observed, as had Harcourt and Esson, that theoretically the reaction is never complete, approaching the maximum percentage of conversion only at infinite time. The 3 reaction curves were found to follow the theoretical curve up to about 80 per cent of inversion, but afterwards there is a decrease in rate of reaction. O'Sullivan and Thompson were unable to account for this behaviour, although they pointed out that Miller had shown the products of reaction to be strongly opposed to further inversion.²

1 O'Sullivan and Thompson, op.cit., 841.

2 O'Sullivan and Thompson, op.cit., 837.

PLATE I. THE TIME CURVE OF THE ACTION OF INVERTASE ON CANE SUGAR



(b) Influence of the proportion of Invertase present

This part of their investigation caused the authors to carry out 'hundreds of experiments' because initial results were incomprehensible. They concluded that the time necessary to achieve any given percentage of inversion, is inversely proportional to the amount of inverting agent present.

(c) Influence of Temperature

O'Sullivan and Thompson had observed that the slightest alteration in the temperature caused considerable variation in the speed of the reaction, and their experiments were carried out using an automatic temperature controlled water bath.¹ But, in order to derive a theoretical model, they assumed that Harcourt's general observation - that for every 10° increase in temperature, the rate of change is approximately doubled - was a law. This was, of course, not true. As we will see in the section on time and temperature, the degree of change in different reactions varies enormously with different temperature ranges. Their curve, not surprisingly, only approximately followed the theoretical model.

(d) The Influence of Foreign Substances

O'Sullivan and Thompson observed that, if an inversion reaction is stopped with only a small amount of alkali, examination of the reaction by a polarimeter appeared to indicate that the 'killing' of the invertase was not instant but required time for its completion.

1 O'Sullivan and Thompson, op.cit., 841,846.

The authors also investigated other factors, such as the influence of the concentration of the sucrose solution, and the effect of varying amounts of acid and alcohol on the reaction system. In the case of acid, it was discovered that whilst minute amounts greatly benefited the reaction, larger amounts were detrimental. Thus, at every specific temperature, the optimum quantity of acid to be added had to be determined individually. Alcohol, by comparison, acted as a 'poison'.

(e) Comparison of the laws governing Inversion with Harcourt's laws

As a result of their detailed analysis of inversion, O'Sullivan and Tompson concluded that for the cases considered - the rapidity of reaction, the influence of amount of invertase, the influence of concentration of solution, the influence of temperature, and the influence of foreign substances - only the third case investigated, and parts of the others, showed any deviation from Harcourt's laws. The reasons for these deviations, they thought, were due to differences in the reacting systems - Harcourt's laws were formulated using a comparatively dilute inorganic solution, whereas inversion solutions were concentrated and viscous.¹

Their conclusion was significant, since it established their aim - to see whether enzyme-catalysed reactions could be distinguished from ordinary chemical reaction:

1. O'Sullivan, Tompson; op.cit., 850.

From this we do not hesitate to draw the conclusion that the action of invertase on cane-sugar is governed by laws similar to those which govern simple inorganic reactions, and therefore we may safely conclude that it is a simple chemical action, differing in no important way from the reactions of inorganic substance, and that there is no reason whatever for supposing that vital force enters in any way into the action.¹

As in the work of Harcourt, O'Sullivan and Thompson found that in establishing their laws of reaction the time factor was the most convenient one for expressing changes in varying functions e.g. the intensity of the activity of samples of invertase. This was facilitated by their discovery that the time that was necessary for a sucrose solution to reach a given percentage of inversion was in inverse proportion to the amount of invertase present. To test the inverting power of a given solution of invertase reaction with time, the authors used the expression $\frac{1}{t} = k$, where k is the number of minutes that the invertase preparation takes to do a certain standard amount of work. They examined changes on the same solution over a period of two years. Within the limits of experimental errors, and under widely varying conditions, they were able to establish that the activity of samples of invertase remained remarkably constant under these varying conditions.²

1. O'Sullivan and Thompson, op.cit., 865.

2. O'Sullivan and Thompson, op.cit., 869.

O'Sullivan and Tompson's experiments on the inversion of sugar are interesting from several angles. The inversion of sugar is a remarkably straightforward case of gradual chemical change, proceeding at a measurable rate, which, it may be recalled, was one of the chief criteria for which Harcourt searched so diligently. The same experiment had been chosen by Wilhelmy in 1850 for the first quantitative study of the rate of chemical change. The rate of change was easily controlled and could be stopped at will, again with a minimum of complications. At the outset of the experiments, O'Sullivan and Tompson's aim was to establish as accurately as possible, whether the general behaviour of enzymes as a whole, recognised as being an important group in the function of life, was unique or whether they conformed to ordinary chemical laws. One theory prevailing at the time maintained that the living organisms by which enzymes are formed (e.g. yeast) imparts to these latter bodies a certain definite 'vital force'. This force is stored up in the ferment until it comes in contact with the particular substance upon which it is intended to act, and consequently brings about a change. This change continues for a period of time until the whole of the vital force is exhausted. At this stage, the ferment or enzyme, though still left, is now 'dead'. By means of the series of experiments carried out by O'Sullivan and Tompson, it was clearly demonstrated that enzymes, as exemplified by invertase, had very specific characteristics which could be quantified and that these quantified properties obeyed established chemical laws. These chemical laws were those laid down by Harcourt and Esson in their studies on a totally different reaction system from that of sugar inversion - complex, inorganic and

totally without reference to any innate 'vital force.' Thus if these two different systems, one organic, the other inorganic, obeyed similar laws, enzymes may be supposed, by induction, also to be chemical substances possessing specific modes of action. Kinetically, they were indistinguishable.

Their results also demonstrated, at the same time, that these enzymes (or ferments) functioned in an identical manner to ordinary catalytic processes.¹ Thus a small amount of invertase was capable of inverting very large quantities of sugar and remained itself unaltered at the end of reaction.

O'Sullivan and Thompson's method of induction was based on the assumption that Harcourt and Esson's laws were truly of general chemical applicability. In fact, their strict adherence to Harcourt's laws extended to a questionable degree. Their theoretical temperature-rate curve, on which they based their subsequent experimental results, for instance, was derived by simplistically assuming that a 10° temperature rise doubled the reaction rate. Harcourt and Esson had not intended this to be a law, but merely a corollary of their observations. Nevertheless, O'Sullivan and Thompson's results were of considerable value in helping to establish what was described, a quarter of a century later as 'new chapters in biochemistry'.² Indeed in 1915, Arrhenius asked the very same question as had prompted O'Sullivan and Thompson's work - whether living matters obey

1 Berzelius had, as early as 1848, pointed to the analogy between catalytic action and fermentation, as had Schönbein. For references see J.W. Mellor; Chemical Statics and Dynamics, London, 1904, 355.

2 S. Arrhenius, Quantitative Laws in Biological Chemistry, London, 1915, p.1.

the same fundamental quantitative laws as those which govern the reactions of inanimate matter.¹

In another area, Walker and Hambly were to apply the results of Harcourt and Esson's work to the study of the transformation of ammonium cyanate into urea in 1895.² The study, inspired by Wöhler's discovery, (almost 70 years earlier), that the transformation occurred spontaneously, was made feasible because quantitative methods for estimating the amount of ammonium cyanate and urea in the solution, at a specific time, were by then available. Liebig and Wöhler had noted that, whilst the change in the transformation took place immediately on boiling the aqueous cyanate solution, it was gradual when the solution was left to evaporate in the air or by gentle application of heat.³ Walker and Hambly thus considered that the course of the reaction could be followed at different temperatures, provided that a method could be found to estimate the amount of change at any given instant. Their method utilized the fact that silver nitrate has no action on urea, whereas with ammonium cyanate it yields a silver salt practically insoluble in cold water, which could then be estimated by titration with standardized ammonium thiocyanate solution.⁴ Their experimental results, measured at different temperatures, were used to calculate velocity constants,

1 S. Arrhenius, op.cit., 19.

2 J. Walker, F.J. Hambly, Trans.Chem.Soc., 1895, 67, 746.

3 J. von Liebig, F. Wöhler, Ann.Phys.Chem., 1830, 20, 393.

4 J. Walker, F.J. Hambly, op.cit., 747.

following closely the methods developed by Harcourt and Esson. Walker and Hambly wrote :

Before Guldberg and Waage had formulated and applied in all directions the law of mass action, it had been shown by Wilhelmy and by Harcourt and Esson that when one molecule was transformed into another, the rate at which this transformation occurred was expressed by a logarithmic formula, which is deduced from the general law.....¹

It would appear, from their results and their method of analysis, that by this time the application of rate studies to the process of chemical change had become a fairly familiar procedure. What is very outstanding in their work is the application of their rate measurements to establish a mechanism for the cyanate-urea transformation, a mechanism for which they were forced, not unexpectedly, to conclude 'that the production of urea from ammonium cyanate does not proceed in so simple a way as we might be disposed to imagine'² Even over 80 years later, the mechanism for this reaction has not been entirely resolved.³

1 J. Walker, F.J. Hambly, op.cit., 752.

2 ibid, p. 753.

3 For an interesting historical account of the cyanate-urea transformation mechanism, see J. Shorter, Chem.Soc.Rev., 1978, 7, 1.

2.4.6. (a) Time and Temperature

The dramatic effect of temperature changes on the rate of chemical reactions was a factor noted very early on, by a large number of investigators. Wilhelmy, in 1850, was probably the first to give a mathematical relation between temperature and the velocity M of a chemical reaction which he expressed as

$$M = KB^t(1-xt) \text{ where}$$

t = temperature, K , B , x = constants.¹

It was observed that the temperature at which reactions proceed was of specific character. Pictet² recorded that sulphuric acid did not react with sodium hydroxide at -125° , but as the temperature rose to -80° , reaction began. With potassium hydroxide, no reaction occurred below -90° ; concentrated ammonia and sulphuric acid are unreactive below -65° . Mellor pointed out that it could not reasonably be assumed that there is no chemical reaction at these low temperatures, merely that the time factor involved was very great.³ The point at which reactions begin varies for different systems, so that the actual temperatures are relative. Thus, though phosphorus does not react with liquid oxygen at a temperature of -180° , it was shown by Moissan and Dewar that solid fluorine and liquid hydrogen combine with explosive force at a low temperature of -252° .⁴ By comparison, it was well known that hydrogen and

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1. L. Wilhelmy, *Ann. Phys.*, 1850, lxxi, 413, 499; Ostwald's Klassiker, 1891, 24
 2. R. Pictet, Compt. Rend. 1892, 115, 814
 3. J. W. Mellor, op. cit., 411
 4. H. Moissan and J. Dewar, Compt. Rend. 1903, 136, 641, 785

oxygen could be kept in a vessel over mercury at room temperature for an indefinite length of time without any noticable changes. In a series of experiments, Meyer and Raum showed that changes in the gases occurred, albeit relatively slowly, under different conditions of temperature, and time.¹ Thus on heating the gaseous mixture for 10 days at 300°, the formation of water could still not be observed, but on continuous heating for 65 days, at the same temperature, water was formed. Again, at 100°, even though the heating was continued for 218 days and nights, no change could be detected. In essence, the phenomena of temperature and time were interdependent. As Mellor put it:

"there is nothing remarkable in the fact that a reaction may be so slow that, at ordinary atmospheric temperatures, the amount of change in a number of years is less than that produced in a few moments when the temperature is elevated a few degrees more".

Even at temperatures for which no chemical change is observable. it is totally feasible that the rate of reaction could be found if time were infinitely extended. Indeed, this was the basis of many early alchemical ideas of time. Meyer referred to the lowest or minimum temperature at which a given system will react perceptibly as "the temperature of reaction".²

1. W. Raum, V. Meyer, Berichte, 1895, 28, 2804

2. L.Meyer; Dynamik der Atome, Breslau, 1883, 417

The explanation for this temperature of reaction is directly related to another phenomena which occurs at the beginning of chemical change, the period of initial acceleration or induction. This will be discussed in a later section. Berthelot believed that the reasons for the observed behaviour lay in a "passive resistance" which had first to be overcome by the application of energy or "travail préliminaire".¹

The influence of temperature (or energy) on the course of chemical change thus raised several interesting questions. For, the general theory, as also observed experimentally, showed that the influence of temperature was a continuous one. These views do not allow for the possibility of sudden accelerations in the reaction, and introduces the hypothesis that if a reaction occurs at any given temperature, it will also proceed at any other temperature, although with a different velocity.² Close examination of reacting systems, however, showed categorically the existence of, not only a specific temperature at which a reaction began, but a period of increased velocity at the start of chemical reactions. Yet nothing at all could be said about when the reaction actually stopped. The course of chemical change was undisputably time-dependent, but little, or nothing, could be determined about either the beginning or the end of the change.

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1. M. Berthelot, Péan de Saint Gilles, Ann. Chim. Phys. 1862, 3, 66, 26
 2. J. H. Van't Hoff, Studies in Chemical Dynamics, London, 1896, 136

Among the many factors influencing the rate of chemical change first considered by Harcourt and Esson in their investigations was the effect of temperature - it proved also to be the most elusive. In their paper of 1867, Harcourt and Esson had concluded:-

... the most important condition of the change whose influence is still undetermined is that of temperature, for this condition intervenes under all circumstances of the reaction, and, indeed, in all chemical changes whatever.¹

They observed that in the reaction between hydrogen peroxide and hydrogen iodide, the rate increased by a factor of 15, when the temperature was raised 40°C.² Their attempts to resolve the problem of temperature/rate of chemical change were to span 45 years and appears to have raised more controversy than any other aspect of their rate studies, as we shall see.

The law connecting chemical change and temperature was given by Harcourt and Esson in their Bakerian Lecture of 1895 in the form

$$\frac{\alpha_t}{\alpha_0} = \left(\frac{272.6 + t}{272.6} \right)^m$$

where α_t , α_0 are the rates of reaction corresponding to temperature t , t_0 , and m an experimental constant..³

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1. Roy. Soc. Proc., 1867, 15, 262-265
 2. ibid.
 3. Phil. Trans. 1895, 186A, 860.

This relation appears to have been derived empirically using data from a large number of experimental measurements carried out by Harcourt. In the account given, it is not easy to deduce how Esson actually obtained this equation, since, although the method of analysis is outlined, the reasoning behind the mathematical deduction is not given. It must be said that Harcourt and Esson are guilty, scientifically speaking, of making no rigorous interpretation of their equation, although they considered it to be of significance. The reasons for this are, perhaps, complex. Both Harcourt and Esson, by this time, 1895, were well advanced in years and no longer working together in the environment of Oxford. Discussion and communication therefore presented considerable difficulty. But a far more important factor was that, for some strange reason, Harcourt and Esson had long avoided consideration of their own work in relation to those of other contemporary chemists, such as Arrhenius, who had, some years earlier, also derived a rate/temperature relationship. The result of this somewhat insular attitude to science, which seemed to have dominated Harcourt's chemical career at Oxford, may indeed have had far-reaching, and unfortunate, consequences. By not showing a true understanding of other important work on related studies, their own results took on much less significance than might otherwise have been the case.

To return to Harcourt and Esson's rate/temperature equation, Esson concluded that when $t = -272.6^{\circ}\text{C}$, the rate of change would be nil. At this point, which is close to the absolute zero temperature of -273°C , Harcourt and Esson

believed that the atoms would be at rest and no contact between any kinds of matter would bring about chemical change. Thus, within the limits of experimental errors, the zero of chemical change coincides with the zero of absolute temperature. The expression may also be written,

$$\frac{\alpha_t}{\alpha_0} = \left(\frac{T}{T_0} \right)^m \quad \begin{array}{l} \text{with } T_0 = 273 \\ T = t + 273 \end{array}$$

valid over the experimental temperature range 0-50°C. This equation, then, established that the relation between amount of chemical change at a given temperature and the absolute temperature is independent of the unit in which each of these quantities is measured. The value of m , as defined by Harcourt and Esson, was found to be a constant for a given experiment at different temperatures.¹ These equations, relating the rate of chemical change to temperature, were made the subject of a special paper more than 17 years later,² in which the previous results, published in the Bakerian Lecture, were summarized:

(a) the increase of rate due to increase of temperature could be nearly represented for equal increments of temperature by geometrical progression. More generally, Harcourt and Esson observed, as had Van't Hoff, that a major characteristic relating velocity of reaction and temperature was that if the temperatures form an arithmetical series, the rates of change at these temperatures would form a

1. Phil. Trans., 1895, 186A, 861.

2. Phil. Trans., 1913, 212A, 187-204

geometrical progression.¹

(b) the rate of reaction was approximately doubled by each rise of 10° in the temperature of solution. It may be pointed out that Harcourt and Esson had confined their major studies to homogeneous reactions.

(c) the rate of change k_t , k_0 at temperatures t° , 0°C was given by

$$\frac{k_t}{k_0} = \left(\frac{273+t}{273} \right)^m$$

with m a constant for each particular case of chemical change.

(d) the implication of this last equation was that at -273° , there would be no chemical change. Actually, the same conclusion can be achieved by plotting experimental velocity results against absolute temperature. The curves obtained can be shown to converge towards zero velocity at absolute zero. This implies that, theoretically, reactions will not cease absolutely at any temperature before absolute zero. However, it does not appear that the theoretical derivation of a zero chemical point was achieved by anyone before Esson⁷.

Harcourt clearly felt that Esson's discovery of the zero point of chemical change was fundamentally important, and that the result had not been sufficiently appreciated -

1. Esson points out that Berthelot appears to have been the first to use this in 1862; see also J. H. Van't Hoff: Studies in Chemical Dynamics, London, 1896, trans. by T. Ewan, 124

in his words it had "attracted less attention than it deserves".¹

The theoretical implications of this natural law, as Harcourt called it, is worth considering briefly.⁴ The idea of a zero point of chemical change is an interesting one, corresponding, perhaps, in a static manner, to the state of dynamic equilibrium, and by, direct analogy to be a state "independent of time". Contemporary chemists of the day who wrote of Harcourt's work, commented upon this discovery as being notable, but it is uncertain what true significance was placed upon this new law at that time, if any.² Even in retrospect, some 80 years later, the practical use to which this revolutionary idea could be put is still doubtful. By contrast, the discovery of the absolute zero of temperature relating to the behaviour of gases was a discovery of enormous consequence in the physics of gases and has been the subject of much discussion by both physicists and historians of science alike.³

It is difficult to assess fully the value of this contribution to chemistry, made by a mathematician, even within the field of modern physico-chemical science. One reason for this, as far as the theory of chemistry is

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1. Phil. Trans., 1913, 212A, 188
 2. H. B. Dixon wrote of this discovery in his obituary of Harcourt: Proc. Roy. Soc., 1920, A, XCVII; see also Proc. Roy. Soc. 1917, 93, LIV
 3. For example see: S. Brush, The Kind of Motion called Heat, North Holland, 1976, 23
 4. Harcourt himself confessed he did not understand the physical meaning of the formula, see later.

concerned, is that the latter, by definition, is the study of the process of change. The use of a law which defines a specific point at which no chemical change occurs belongs, perhaps, to other realms.

In the paper of 1913, read before the Royal Society on May 9th of the previous year, the temperature dependence of rates of chemical change was repeated afresh. The system chosen for study consisted of solutions of ferric chloride and stannous chloride which, when mixed, form ferrous chloride and stannic chloride.¹ It is not clear why Harcourt chose this particular pair of solutions, although the aim was to measure the influence of temperature on gradual chemical change. Chemical systems displaying a rate of change sufficiently slow so as to permit measurements were not easy to find and were the subject of much investigation by Harcourt in his previous work, as we have already seen. The experimental procedure in this case involved the measurement of time intervals, during which the reaction between the 2 solutions was completed, as indicated visually by colour changes, at different temperatures. The presence of potassium sulphocyanide ensured that the colour change, from blood-red to a pale colour at the completion of the reaction, was sufficiently dramatic to be experimentally measurable. To achieve this, Harcourt used dark and pale standard solutions as colour controls, in what he describes as a "police-trap" method. This permitted time intervals to be measured when

1. This reaction had been studied in some detail by A. A. Noyes, Zeit. Phys. Chem., 1895, 16, 546; ibid., 1896, 21, 16; Technology Quarterly, 1895, 8, 90; L. Kahlenberg, Am. Chem. J., 1894, 16, 314; F. L. Kortright ibid., 1895, 17, 116.

the change under investigation passed through these two control points. "The observer looked at the two, watch in hand, closing his eyes at intervals for a few seconds to get a fresh impression, till the colours seemed indistinguishable, made a mental note of the time, and continued to watch till the contents of the reagent tube seemed the paler of the two."¹ Exactly the same routine was followed for each observation, differing only in the temperature of the liquid.

The experimental difficulty of such a procedure is hard to imagine, complicated by the method used for maintaining a constant temperature during each set of chemical change. This was done by placing the reagent tube on an iron tray, covered by white paper, which was heated beneath at one end by a small gas flame, while the liquid was stirred by the passage of large bubbles of carbonic acid from an inverted thistle-funnel. By moving the tube nearer to or further from the heated end of the tray, or by moving the gas burner, the mean temperature of the liquid was regulated. Harcourt maintained that during intervals varying from five minutes to three-quarters of an hour, the mean temperature of the liquid could be controlled to within about 0.05°C .² Compared to modern thermostatic control, which in temperature/rate-experiments, is vital, Harcourt's method does not seem really viable. He himself admitted that the method did not admit of an accuracy approaching that of observing the colour change

1. Phil. Trans., 1913, 212A, 189

2. Phil. Trans., 1913, 212A, 189

in his previous iodide/starch determination.¹ The observations with the chloride solutions, under the experimental procedure briefly outlined, nevertheless provided Harcourt and Esson with data sufficient, within their limits of experimental error, to test further the formula already established in their Bakerian Lecture. Esson assumed that the rate of chemical change was related to the concentration y , and the time x by a relation of the form

$$f(y_2) - f(y_1) = kx$$

In his words, "the time x is the observed time during which the potential chemical energy expressed by $f(y_1)$ had changed to the potential chemical energy expressed by $f(y_2)$ ".²

In Harcourt's experiments, this change of energy was indicated by the passage of the solution from one colour to another. They further assumed that, at different temperatures, this change of energy was constant. Thus if k , k^1 are the rates of change at temperatures T , T^1 respectively, and x , x^1 are the corresponding observed times,

$$f(y_2) - f(y_1) = kx = k^1 x^1$$

the relation $kx = k^1 x^1$ was thus independent of the form of the function $f(y)$, and the method of observation equally applicable to unimolecular and multimolecular reactions. When this was assumed, their previous equation

$$k^1/k = (T^1/T)^m$$

became very simply

$$x/x^1 = (T^1/T)^m \quad (I)$$

1. Phil., Trans., 1913, 212A, 190

2. ibid., 194

that is, the time (x) of chemical change was inversely proportional to the temperature T , from which the experimental constant m could be calculated.¹ Experimentally, x , x^1 represented consecutive observed values of the times at temperatures $T=273+t^0$ and $T^1=273+t^{10}$. Esson firmly believed that the method of experiment was capable of giving very accurate results.²

For each set of experimental observation, Harcourt used an aqueous solution, 80c.c in volume, consisting of feric chloride FeCl_3 , potassium sulphocyanide, KCNS , stannous chloride SnCl_2 , and hydrogen chloride (hydrochloric acid HCl). As he had done previously in his earlier work, Harcourt took measurements using varying amounts of the reactants, and determined the proportions which gave convenient rates of change over the whole range of experimental temperatures. The values of m calculated over eight different temperatures differed in excess of 10%, reflecting the complexity of the system under investigation, assumming that Esson's derivation of a constant value for m was valid.

As was the pattern set in several previous papers, the author of this publication was Harcourt, to which was added an Appendix by Esson. In this appendix, Esson applied his formula (I), previous page, to the experimental results of several other authors to test his basic assumption that m was a constant at different temperatures for a given experiment

1. Phil. Trans., 1913, 212A, 195

2. ibid., 195

Many of these experiments had been quoted by Vant' Hoff in his publication of 1896 and, in addition, Esson chose several sets of data, taken at random, which had been published during the few years previously. The results of applying formulae (I), to these diverse chemical systems showed that, whilst several of the experimental results agreed with Esson's theory (that the value of m should be constant for a given set of experimental conditions), others did not.¹ Esson was unable to explain these discrepancies but expressed his intention of discussing at some future date all the experiments upon the subject, and hoped, with the aid of Harcourt, to discover an explanation for the variations in m values observed. This hoped-for concerted effort was not to be. Esson died three years later.

By this time, Harcourt's investigation of time factors in chemical change had no doubt vastly increased his understanding of how these changes occurred. But in the case of temperature influence on the rate of chemical change, this was a problem which Harcourt himself felt remained unsolved, even after a lifetime of experimental enquiry:

....the author ventures to express the hope that it may attract the attention and pass into the hands of some younger chemist. The mode of working adds to the usual interest of research and the particular excitement which attaches to all observations and

1. Phil. Trans., 1913, 212A, 202

prediction of time, sporting or
scientific, whether it be of the time
of a race or of the moment of an
occultation.¹

At the time of the publication, Harcourt was in his 79th
year.

1. Phil. Trans., 1913, 212A, 193

2.4.6. (b) Problems and Criticisms

From letters which have survived, now in the libraries of the Royal Society and Balliol College, Oxford, we learn that the relation between temperature and chemical change was a subject which had special significance for Harcourt. It was work for which he felt the credit belonged more correctly to Esson. Interestingly, this particular aspect of their work caused them more problems, and perhaps criticism, than had any previous part of their 50 years work.

Writing to Sir John Conroy in 1894, from his home in the Isle of Wight (to which he eventually retired from Oxford), he said:

My chief occupation has been finishing a paper which ought to have been finished 20 or more years ago! I have finished it now, except a possible summary, and have sent it off to Esson for correction and approval, the former being especially required by my efforts at algebraic or graphic representations.¹

The paper to which he referred was the Bakerian Lecture, which appeared a year later (1895). In a rare assessment of his own work, Harcourt continues:

I think the paper of the work described

1. The Conroy Papers, Balliol College library, Oxford, (IB, Bundle 14)

rather good - it was so long ago I can almost judge of it from outside - but much the best bit is Esson's description of our temperature experiments.¹

To Conroy, he communicated Esson's equation relating chemical change and temperature

$$\alpha_{t'} = \alpha_t \left(\frac{273+t'}{273+t} \right)^m$$

Seventeen years later, writing to Larmor, secretary of the Royal Society, in connection with the publication of the temperature/rate of chemical change work in 1913, he continued to maintain:

I suggested to him (Esson) that as his contribution is of much larger scope than mine, it ought to appear as the principal paper, and mine might follow as a recent piece of work.²

The referees did not concur with this, and the paper appeared in the form described. This paper produced some controversy, for on 30th April 1912, Harcourt wrote again to Larmor, clearly in answer to criticisms made by the referees. The text of the letter sheds much light on the temperature/rate work, as well as some of the problems relating to joint efforts lasting over half a century, when one (Harcourt) was proficient only in solving chemical problems and the other (Esson) in mathematics:

1. Conroy Papers, op. cit.

2. Royal Soc. Library; Harcourt, A.G.V. (No. 12157)

My dear Larmor,

Esson, good man though he is, has erred in writing his appendix. Out of a multitude of chemical changes sufficiently gradual for their rate to be measurable, and out of a certain number of these whose change is so marked that a small fraction of a manageable whole is observable, only a few are so simple as to give a pure result.

In the particular case of variation with temperature, it is often the nature, as well as the rate, of the change which is altered. I have not read the papers from which Esson has derived the tables with which he deals, nor I think has he. I believe they are taken from a summary of such observations in a book by Mellor and some other similar source.

This being so, it is not surprising that he finds his formula inapplicable in a majority of cases. The error is not, as I believe, in the formula, but in there not having been a rejection, on chemical grounds, of cases in which the nature of the reaction, or the proportion of two independent reactions, was likely to vary with the temperature of the liquid... this is not my first experience of physicists erring through unacquaintance

with the complexity of chemical changes.¹

Harcourt expressed his helplessness to making any further contributions to the dilemma, as the paper was already so close to the publication date. At the time of writing, Harcourt was in Norfolk, far from the laboratory facilities of Oxford, or London. He confessed to Larmor, that he did not know what to do.

Through lack of mathematics, I cannot judge of the probability of Esson's formula. I do not see the physical meaning of the exponential formula $(K_t/K_{to}) = (T/To)^m$, and I find by experimental arithmetic (which is my sole resource) that I can take for To values differing widely from 273° (abs.l.) with a corresponding variation of K_{to} and of m and get numbers as concordant with the experimental results as those calculated secundum artem My faith rests on Esson's calculation of the constants of his equation and the emergence of the figure 272.6, upon the close agreement over a long series of observations....²

Despite these discrepancies, the referees decided that the paper remained worthy of publication in the Philosophical Transactions, with the proviso that Esson should discuss

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1. Royal Soc. Library, Harcourt, A.G.V. (No. 12156)
 2. Royal Soc. Library; Vernon Harcourt, A.G. (12156)

his law in relation to the work of Trautz and Volkmann.¹

In the light of the problems and complexities relating temperature and rates of chemical reactions experienced by Harcourt and Esson, it is interesting to look briefly at other work of the time, in this field.

The very dramatic increase of reaction velocity caused by a rise in temperature had been noted experimentally in a large number of cases, particularly in the last decade of the 19th century. Many of these results were included in both Van't Hoff's important work of 1884, Studies in Chemical Dynamics and Mellor's later publication, Chemical Statics and Dynamics (1904). Thus Mellor notes that barium formate decomposes twice as rapidly at 330° as it does at 260°; the inversion of sugar proceeds five times as fast at 55° as it does at 25°; the transformation of dibromosuccinic acid into bromomaleic acid goes three thousand times as rapidly at 101° as at 15°². The now familiar general rule, that the reaction rate of homogeneous solutions approximately doubles for a 10° temperature rise, was noted by Harcourt and Esson in their Bakerian lecture,³ and also by Van't Hoff.⁴ The influence of temperature on

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1. Phil. Trans., 1913, 212A, 203: "June 15 - the referees of this paper have asked the author to discuss, with reference to the law here advocated, the experiments of Trautz and Volkmann "On the Saponification of Esters", 'Zeit Phys. Chem', 1908, 64, p. 53-88; 1909, 66, p. 496; 67, p. 93; 68, 295 "
 2. J. W. Mellor, Chemical Statics and Dynamics, 1904, London, 383-384
 3. Phil. Trans. (Series A), 1895, 186, 817
 4. J. H. Van't Hoff: (Études de Dynamique chimique, 1884) Studies in Chemical Dynamics; London 1896, trans. by T. Ewan, 125

chemical equilibrium was given by Van't Hoff in his publication of 1884, as

$$d \frac{\log K}{dT} = \frac{q}{2T^2}$$

where K is the equilibrium constant and q the quantity of heat evolved at the absolute temperature T ($T=273+t^{\circ}\text{C}$).¹

More generally, the relation between the constant K and temperature may be written

$$d \frac{\log K}{dT} = \frac{A}{T^2} + B$$

where A and B are constants.²

This equation relating the constant K and temperature, derived by Van't Hoff from thermodynamics, raised two fundamental problems. First, it applies strictly to the end state of a chemical change i.e. conditions at equilibrium, and hence does not provide the desired relationship between actual reaction velocity and temperature, as Van't Hoff himself pointed out.³ Since the equilibrium state is purported not to involve time factors, the equation is useless when predicting the time required in achieving this state.⁴ Secondly, it is clearly an over-simplification to assume that the factors A, and B are constants, since the quantity of heat evolved or absorbed, during chemical reactions, changes

1. J. H. Van't Hoff, op. cit., p. 132. Mellor, in his Chemical Statics and Dynamics, p. 387, points out that A. Dupré had used a similar expression in his Theorie Mécanique de la chaleur, Paris, 1869, 97
2. Van't Hoff, ibid., 123
3. Van't Hoff, Ibid., 123
4. Mellor comments on this in his book, see ref. 1 above 387

with temperature. This dependence of A, B on temperature remained unresolved in Van't Hoff's equation.

Furthermore, the explanations for the very large rate change with temperature could not be found in the existing kinetic theory. As Arrhenius pointed out, according to the kinetic theory of gases, the velocity of the gas molecules changes only by about $\frac{1}{6}$ per cent of its value for each one-degree rise in temperature and the frequency of collisions increases in the same ratio.¹ He wrote:

It is difficult to say with certainty how large is the corresponding change in the case of liquids, but it is suggested that it is similar to that in gases. Even if the assumption that the velocity of the solute molecule changes by $\frac{1}{6}$ per cent per degree is not accepted, it must at least be agreed that the difference between this value and the observed 10 to 15 per cent per degree is much too large for it to be assumed that the increase in the number of collisions of the reacting molecules is the reason for the increase in the reaction velocity with the temperature.²

Arrhenius investigated the inversion of cane sugar, and as a first approximation of Van't Hoff's equation,

1. Zeit. phy. chem., 1889, 4, 226

2. ibid.

he assumed the simplified form

$$d \frac{\log K}{dT} = \frac{A}{T^2}, \text{ putting } B=0$$

This did not solve the dependence of A, B on temperature, for as Arrhenius clearly realised, the dependence of A, B on F(T) could be anything at all.¹

Since the increase of the velocity of chemical reactions with temperature could not be explained by any change in the physical property of the solution, Arrhenius postulated that the molecules of cane sugar were of two kinds, passive and active. The quantity of "active cane sugar" increases rapidly with rise in temperature, by about 12 per cent per degree. This transformation of inactive (passive) molecules to active types could be envisaged by a rearrangement of atoms. At equilibrium, and using Van't Hoff's equation, Arrhenius gave the relation for rate constants K at temperatures T_1 , T_0 as

$$K_{T_1} = K_{T_0} e^{q(T_1 - T_0)/2T_0 T_1} \quad 2.$$

This equation was re-written in the general form

$$K = Ae^{-E/RT}$$

Where A, E are constants and R is the gas constant. This equation is now recognised as the most fundamental relation between rates of reaction and the temperature, with E as the activation energy. However, its significance was probably not immediately recognised, for Mellor considered Arrhenius's view as but one of many expressions "out of the infinite number of equally effective formulae which might

1. Zeit. phy. chem., 1889, 4, 226

2. Zeit. phys. chem., 1889, 4, 226

be proposed".¹ In 1904, the generalization or law connecting the thermal value of a reaction with the temperature had yet to be discovered.² The understanding of the temperature dependence of reaction rates required first an understanding of how the reactions were actually proceeding and of why they were proceeding in this manner, at a molecular level. In fact, at the time of Harcourt and Esson's work, the two fundamental ideas necessary to provide such theories already existed - the theory of atoms in motion hypothesized by Williamson (as discussed earlier), and the idea of energised molecules, proposed by Arrhenius.

Harcourt and Esson realised, of course, that some explanation existed for the discrepancies found in their results, when applied to a broader spectrum of chemical reactions. They sought for underlying reasons within the complex chemical side-effects which they were unable to include in their analysis, as Harcourt indicated in his letter to Larmor. Esson thus felt it was advantageous to make a more general statement of his law. Generally, he concluded, when studying the effect of one phenomenon A upon another B, which mutually influence each other, *one cannot know* the complex interaction between A and B formed a chain process whose overall function was unknown. In the light of this, Esson assumed that when this chain process was uniform, the ratio of the increase per cent in B to the increase in A is constant, and further assumed that if the chain is not uniform, the ratio, though no longer

1. J. W. Mellor, op. cit., 393

2. ibid.

constant, would still be a measure of the effect of A upon B.¹ Using this argument in the analysis of their experimental results, in which extreme care had been paid to eliminate possible experimental errors, Esson felt confident that they had arrived at "the true relation-between temperature and chemical change".²

Nevertheless, Harcourt and Esson did not satisfactorily account for the reasons as to why temperature should have such paramount effects on rates of change, nor, as we have seen, was their equation capable of very wide rigorous application. Even more important, they appear not to have seriously considered the work of their contemporaries such as Vant Hoff and Arrhenius, in related fields. In their paper of 1912, Harcourt, referring to the papers of Volkmann and Trautz previously mentioned, commented that though the latter authors gave lists of the literature on the subject, they did not include Esson's or his own papers.³ Volkmann and Trautz in fact give Harcourt and Esson's formula but do not discuss it.⁴ In retrospect, this apparent lack of

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1. Phil. Trans., 1913, 212A, 202. Where the mode of influence of one kind of energy upon the other is unknown, Esson expressed the measuring of the influence of A upon B as $m = (B^{-1} dB)/(A^{-1} dA)$. In a paper delivered to the 5th International Congress of Mathematicians, held in Cambridge in 1912, Esson proposed to use this relation, which he had derived from chemical considerations, for other, social or economic problems. Thus, he indicated, in studying the relation between unemployment and pauperism, the proper cause might be to take the ratio of the increase per cent of pauperism to the increase per cent of unemployment as the measure of the effect of one upon the other. /Proceedings of the 5th International Congress of Mathematicians, Cambridge 1912, Vol II, 272-3/
 2. Phil. Trans 1913, 212A, 204
 3. ibid., 203
 4. Zeit. Phys. chem., 1908, 64, 57

communication between Harcourt and other workers, especially those in other countries, is particularly puzzling. A similar case, noted earlier, is the almost complete silence between themselves and Guldberg and Waage in Norway. That Harcourt and Esson's work did influence many workers, more especially in England, is clear and will be discussed in a separate section.

2.5 Time Factors Established: Problems and Progress in Rate Studies

2.5.1 Chemical Forces and the Beginning of Reaction Mechanism

The search for an understanding of the forces responsible for chemical interaction can be seen to run continuously through the history of chemistry, as it developed from early alchemy to that of a quantified science.¹ In the thoughts of Newton and in the writings of Berthollet, the problem of chemical affinity remained, however, an elusive enigma. Ideally, the search was for a chemical analogy to existing theories of the forces of nature, in this case, the physical forces. Mills, in his eulogy of 1876 on the first principals of chemistry put it thus:

The mind of Berthollet was clearly impressed with the necessity of reconciling the laws of chemistry with those of astronomy. As he contemplated the evening sky and watched the marshalling of its glorious host, no thought of atoms arose (as in Dalton) with those of distant clusters; but the conviction that the earth's laws are not discrete from those of heaven, and that the principle of celestial attraction must

¹ For an account of Affinity and Theories of Matter see: T.H. Levere, Affinity and Matter, Oxford, 1971; A. Thackray, Atoms and Powers, Cambridge, Mass., 1970

be identical with or animate, the chemical process¹

Yet it is doubtful whether chemists can be said to have ever resolved, completely and satisfactorily, the answers to the problem of chemical affinity. As Todhunter put it:

Men abandoned their attempts at explanation and finally acquiesced in the name Affinity, as simply a description of the phenomena without further analysis²

The middle years of the 19th century, the very period during which Guldberg, Waage, Harcourt, Esson and others³ were pursuing factors affecting the rates of chemical change for the first time, also saw theories of heat and energy being evolved, culminating in the rise of chemical thermodynamics. Although the theory and mathematical expressions for chemical velocity had been developed by direct analogy with Newtonian mechanics, closer examination of reacting substances now encouraged a search for an understanding of complications arising within the chemical system itself. Thus, in the process of developing theories of mass action in chemical reactions, Guldberg and Waage, as well as Harcourt and Esson, had introduced ideas which were later to be incorporated into other chemical theories, for example, the idea of reaction sequence and that of interference due to presence of foreign substances.

1 Phil Mag, 1876 (S.5), 1, 1.

2 Quoted in J.R. Partington, A History of Chemistry, London, 1964, Vol 4, p 587.

3 The law of Mass Action was also established by others e.g. Jellet, see Partington, op.cit., 583.

Nevertheless, the more familiar problems of affinity were still far from being exhausted. The affinity coefficients of Bunsen, now quantified by Guldberg and Waage, at least raised the hopes of some chemists that a better understanding of the elusive chemical affinity could not be too far away. Up to that time, around 1865, it appears that though velocities of moving bodies were well known to be related to the force producing motion, the idea^{of}/relating velocity of chemical reactions with the affinities of reactants had not been established.¹ During this initial period of time studies in chemistry, both Harcourt/Esson and Guldberg/Waage required a physical system from which to embark on their respective studies. Chemical equilibrium, infinitely more complex in its final elucidation than could have been at first conceived, had its origins in the physical analogy of mechanics. But whereas Guldberg and Waage were still searching for the quantification of the elusive chemical affinity, clearly to the very end, Harcourt and Esson, as we have seen, were able to avoid such complications. To explain the nature of their respective chemical systems, both teams advocated theories which were to become the accepted tradition in future studies of chemical reactions: attempts to explain the reason why the substances reacted at the rate, and by the method, they did - their reaction mechanism.

1 M.W. Lindauer, J.Chem.Edn. 1962, 39, 8, 384-390.

It is not difficult to recognise the basis of ideas of 'spheres of action' which emerged in both studies. Berthollet had based his concept of the mass law on the principle of attraction between static bodies - each particle exerted an attractive force on its neighbours, so that the overall effect was directly related to the number of particles in a given area. Guldberg and Waage also proposed a theory of secondary forces acting between all substances taking part in the reaction. But as attractive as the ideas were, these weak forces proved even more elusive than the primary forces of affinity, and had to be abandoned. In comparison, Harcourt and Esson envisaged the explanation that, for their system of permanganate and oxalic acid:

... the dissolved binoxide exists in the fluid in the form of minute spheres upon whose unit of surface is performed a constant action. The total action thus at any moment varies with the surface exposed, and diminishes continually as the spheres, shell after shell, melt away.¹

The problems facing both teams, working in widely separated countries, were very similar. Not surprisingly then, their endeavours in the field of rate studies prompted almost identical feelings:

¹ Chem. News, 1864, 173.

Investigations in this field are doubtless more difficult, more tedious and less fruitful than those which now engage the attention of most chemists, namely the discovery of new compounds. Nevertheless, it is our opinion that nothing can so soon bring chemistry into the class of truly exact sciences as just the researches with which this investigation deals ... a branch of chemistry which, since the beginning of the century, has unquestionably been far more neglected than it deserves.¹

wrote Guldberg and Waage in 1867. It is interesting to compare this with Harcourt's views on the very same theme.²

The idea that the heat evolved during a chemical reaction could be the direct result of chemical forces in action and therefore be a measure of affinity had occurred to several workers, notably the Danish thermochemist Julius Thomsen and to Berthelot. As early as 1854, Thomsen had stated that

every simple or complex action of a purely chemical nature is associated with production of heat.³

1 Études sur les Affinités Chimiques, Christiania, 1867; Ostwald Klassiker, 104.

2 See section of the work on Harcourt and Esson.

3 J. Thomsen Ann. Phys., 1854, 92, 34; Berichte, 1873, 6, 423-8.

Guldberg and Waage were aware of Thomsen's work and in their publication of 1867 discussed the 'chemical heat theory'. The heat evolved in a chemical reaction, they maintained, must depend upon thermal capacities and could therefore not be taken as a true indication of the affinity. Many reactions could not be related to heats of reaction because they were immeasurable. This was true in the case they were studying, the potassium carbonate/barium sulphate reaction. Berthelot's 'principle of maximum work' - which stated that

every chemical change which takes place without the aid of external energy tends to the production of that which is accompanied by the development of the maximum amount of heat.¹

was intended only to imply an equivalence, between heat evolved and affinity, for reactions which occurred spontaneously. Such systems were not particularly useful when studying reaction rates. But his definition of 'chemical heat' referred to that heat which was transformable into work, an idea which emerged later as free energy.²

The dynamic view of matter, intensified by the establishment of the Kinetic Theory of Gases, was also, by this time, being incorporated into chemical thinking. Only three years after Guldberg and Waage's publication of 1864,

1 M. Berthelot, Essai de Mécanique Chimique, Paris 1869, 28.

2 M. Berthelot, Compt.Rend., 1894, 118, 1378.

Leopold Pfaundler, then Professor of physics at Innsbruck, had published a detailed discussion of equilibrium and mass action from a molecular kinetic point of view.¹ With remarkable foresight, Pfaundler carried his theories over to equilibrium studies in gaseous systems. Maxwell's law of distribution of molecular velocities had indicated that, at ordinary temperatures, the proportion of molecules having energies markedly greater than the average was very small but that this increased rapidly with temperature.² Pfaundler, applying this idea to his studies of chemical equilibria, supposed that only those molecules possessing more than a critical energy could undergo chemical change. This idea was later adopted by Arrhenius in his derivation of the relation between rate constant and temperature.³ At constant temperature, only a fraction of the molecules undergo change, and as other molecules are reformed, a state of equilibrium can be established; molecules of compounds were breaking up whilst others were being formed with equal velocity. Thus, according to the Kinetic Theory, the number of collisions of gas molecules per second increases with rise of temperature, but the reaction velocity increases faster, following an exponential form.⁴

1 L. Pfaundler, Ann.Phys.Chem., 1867, 131, 55; 1874, 182.

2 J.C. Maxwell, Phil.Mag. 1860, 4, 19, 22; Phil.Trans., 1867, 157, 49.

3 S. Arrhenius, Zeit.Phy.Chem., 1889, 4, 226

4 J.C. Maxwell, op.cit.,

what of it?

Horstmann, in 1873, used Guldberg and Waage's earlier data on solid barium sulphate and a solution of potassium carbonate, to study the problem of heterogeneous systems.¹ The equilibrium in heterogeneous systems appeared to be independent of the absolute or relative amounts of the solid phases. Horstmann was able to show that this was due to the ratio between the concentrations of sulphate and carbonate remaining constant at constant temperature. These papers by Pfaundler and Horstmann incorporated thermodynamic functions, for the first time, into the study of chemical equilibria.

Guldberg and Waage were well aware of these advances taking place at the chemical front. In 1879, they published a further paper, this time in the German periodical Journal für praktische chemie. The paper developed the law of mass action on the premise of the later theories of molecular motion.² They assumed that the molecules of the compounds reacting possessed different states of energy, and only those possessing sufficient energy were capable of initiating actual reactions, as Pfaundler had suggested. They reasoned:

1 A. Horstmann, Ann.Chem. and Pharm., 1873, 170, 192;
Ostwald's Klassiker, 137

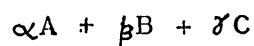
2 J. Prakt.Chem. 1879, 127, 69.

If the number of molecules of A and B in unit volume be denoted by p and q, the product pq will represent the frequency of the encounters of these molecules. If each motion of the various molecules be equally favorable to the formation of new substances, the velocity ... may be made equal to ϕpq , the coefficient of velocity being supposed dependent on temperature. This view, already known from the theory of gaseous dissociation, may now be extended as follows so as to apply to all states of aggregation.¹

To allow for the fact that only certain collisions are effective in initiating chemical change, the velocity was given by

$$v = \phi a^p b^q = k p^p q^q \text{ where } \phi a b = k$$

and a, b represent the fraction of each of the molecules p, q capable of reacting. In this paper, Guldberg and Waage introduced, for the first time, power coefficients which represented the actual number of molecules taking part in the reaction. Thus, if a and b are the number of two different kinds of molecules in unit volume, the number of collisions in unit time is proportional to ab; if all the molecules are identical, then the collisions are proportional to a^2 and for three molecules, to abc or a^3 . They gave the most generalised form for the reaction,



1 C. Guldberg and P. Waage, J. Prakt. Chem., 1879, 127, 69.

the rate expression:



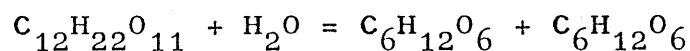
where k is the product of the coefficients. In this later work, Guldberg and Waage still maintained the idea of secondary forces but once again, as they had not the means with which to explain it further, they assumed the effects to be negligible in dilute solution. Although they had advanced the understanding of chemical equilibria to a new level, Guldberg and Waage were unable to take into account such important factors as electrolytic dissociation of salts in solution.

Viewed from a distant perspective, the work of chemists in the second half of the 19th century, including Guldberg/Waage, Harcourt/Esson, Berthelot, Thomsen, Pfaundler, Maxwell, and Van't Hoff, together, represents a radically new and formidable picture of scientific progress in the chemical field. By then, quantified energy factors had certainly been introduced into chemical thinking, as had the kinetic theory. Ideas of chemical dynamics were now established; it only required the mathematical skills of J. Willard Gibbs to create, and for Van't Hoff to describe, the new tool of thermodynamics for chemistry. In one giant step, the understanding of chemical processes, which had escaped generations of experimental chemists, became a fully quantified science. Empiricism became a secondary source, a luxury to have to hand when all else failed. Although Gibbs published his treatise, On the Equilibrium of Heterogeneous Substances in the years 1876 and 1878, the work remained uncomprehended and neglected

for another generation. Van't Hoff's publication of 1884, Études de Dynamique Chimique, on the other hand, brought together the experimental results of many of the pioneers of kinetic studies, including those of Harcourt and Esson, Berthelot and St. Gilles, Guldberg and Waage, and recrystallised them with new insight. It consolidated much of the earlier developments, a necessary step in any sequence of historical events. Chemical progress had, undeniably, come a long way since the beginning of that century.

2.5.2 Order and Psuedo-Order

An important discovery which emerged from amongst the large number of rate studies during the second half of the 19th century was that, frequently, there appeared to be no apparent relation between the number of molecules actually taking part in a chemical reaction and the number of molecules denoted in the balanced equation. Thus the form of the rate law for a specific reaction could not be assumed by direct reference to the stoichiometry of the reaction. For instance, the inversion of cane sugar, first studied by Wilhelmy in 1850,¹ can be represented by the equation



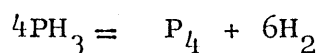
The form of this equation denotes that two molecules, sugar and water are reacting. But, experimentally, it could be shown that the rate of chemical change depended upon the sugar alone, when water was present in excess.

Van't Hoff distinguished between different types of reaction by the number of molecules taking part in the reaction, designating them as mono-molecular, bimolecular or polymolecular.² Although it was recognised fairly early on in the study of reaction rates (by Harcourt and Esson for example) that different relative amounts of reactants in a chemical reaction, as well as the number of reactants, were relevant factors in determining rates of reaction, the

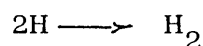
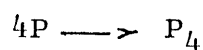
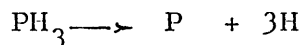
1 Pogg. Ann., 1850, 81, 413, 499.

2 J.H. Van't Hoff: Studies in Chemical Dynamics, London 1896, trans. by T. Ewan, 1, 4.

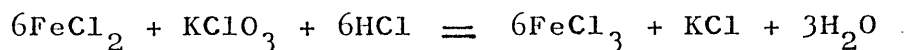
actual form of this dependence only emerged after the accumulation of considerable data. Between the years 1850 (when Wilhelmy published his paper) and the end of the 19th century, a large number of reactions of the bimolecular type were found to behave like unimolecular reactions. Harcourt and Esson showed that this was the case in the reduction of potassium permanganate by an excess of oxalic acid; and again in the reaction between hydrogen peroxide and hydrogen iodide.¹ Van't Hoff demonstrated this for several cases, including the decomposition of phosphine, in which the reaction



was shown, not to be tetramolecular with respect to phosphine as would be expected from the mass law equation, but monomolecular.² The decomposition takes place in several stages,



so that each phosphine molecule decomposes independently of the others. Noyes and Wason studied the reaction



and found the reaction to be trimolecular.³ An increasing number of such studies thus showed that more often than not, such equations gave an entirely false idea of the mechanism of the reactions, only expressing the quantitative aspect of them, as Van't Hoff pointed out.⁴ In 1889, Ostwald and

1 Phil.Trans. 1866, 156, 193; Proc.Roy.Soc. 1865, 14, 470; Phil.Trans. 1867, 157, 117; J.Chem.Soc. 1867, 20, 476.

2 J.H. Van't Hoff, op.cit., 20, 101.

3 Zeit.Phys.Chem., 1897, 22, 210.

4 Van't Hoff, op.cit., 20.

Fuhrmann suggested the use of the terms 1st, 2nd, 3rd...nth order reactions to denote the sum of concentration terms which occur in the differential form of the rate law.¹ This enabled the distinction between the order of rate law, which could be determined only experimentally for each specific reaction, independent of the stoichiometry of reaction, and the molecularity, as defined by Van't Hoff.²

Such a distinction was an important step in clarifying many of the complications which were becoming apparent in chemical systems being investigated. In particular, the realisation that most chemical reactions did not take place by simple, one-step action, but followed a more complex series of such steps, enabled increasing understanding of reaction mechanism to develop.³

Mellor referred to homogeneous consecutive reactions as 'abnormal' reactions and stated the rule now frequently quoted:

1 A. Fuhrmann, Zeit.Phys.Chem., 1889, 4, 89.

2 This distinction was not always understood by many of the early workers. Esson mistakenly referred to his and Harcourt's rate studies as 'unimolecular' when it was clearly bimolecular but of 1st order: Phil.Trans., 1913, 212A, 202.

3 The term 'mechanism', to denote the way in which chemical changes were occurring within a given reaction was in use by 1904. Mellor, in his book Chemical Statics and Dynamics (p.354), wrote 'A detailed description of the characteristics of the enzymes belongs to the sphere of physiological chemistry, we are here mainly interested in the mechanism of the chemical changes which they invoke, because these changes are so closely allied to ordinary catalytic processes'.

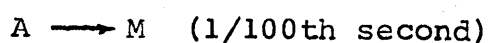
If a chemical reaction takes place in two stages, one of which is considerably faster than the other, the observed order of the whole reaction will be determined by the order of the slower change.¹

Walker, in 1898, had described the phenomena in a similar manner:

....that stage which proceeds most slowly plays the principal part in determining the rate of the whole reaction, being only more or less modified by the other more rapid changes. If these are indefinitely faster than the slow change, their modifying influence will be so slight as to be negligible²

As a general case, Mellor gave the following example:

In a reaction in which substance A forms an intermediate compound M, which, in turn, becomes the final substance B, suppose



If the first stage takes place in 1/100th of a second, whilst the second stage occurs in 1 hour, the overall rate of the reaction actually observed in



is determined solely by the stage $M \longrightarrow B$.³

1. J. W. Mellor, op. cit., 95-96.

2. J. Walker, Proc. Roy. Soc. Edin., 1898, 22, 22-32. (p.24)

3. J. W. Mellor, op. cit., 95.

By the same reasoning, for any chemical change in which a number of fast steps accompany a slow stage, the latter alone still determines the overall speed of reaction. As Guggenheim has pointed out, the stoichiometry of equations may falsely represent the idea of the correct mechanism of the chemical change taking place, and many modern textbooks make similar mistakes in not making this clear.¹ The concept of representational equations expresses merely the quantitative aspect of the change, not necessarily the whole sequence of events, nor the order in which the changes occur. This realisation constitutes a fundamental advance in the theory of chemical kinetics, and as Mellor wrote, established the existence of one of the most difficult aspects of the subject.²

Harcourt and Esson, in their paper of 1864, were the first to attempt a study of the complexities of consecutive reactions.³ Between the time of their work, to the year 1904, the year when Mellor's book on chemical statics and dynamics was first published, the subject was not treated to any further systematic analysis. In Mellor's words:

although Harcourt and Esson's work is so often cited, yet this phase of their work is generally overlooked. The neglect is surprising. But the combination of

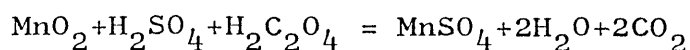
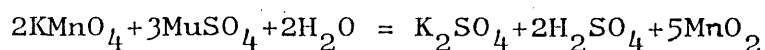
1. J. Chem. Ed., 1956, 33, 11, 544-545

2. J. W. Mellor, op. cit., 95

3. Chem. News, 1864, 10, 171; B. A. Report, 1865, 29; Proc Roy. Soc., 1865 14, 470; Phil Trans. 1866, 156, 193.

mathematical dexterity with the chemical astuteness necessary for the treatment of consecutive chemical reactions is not particularly common.¹

Harcourt and Esson observed an initial acceleration of the reaction between potassium permanganate and oxalic acid in the presence of sulphuric acid and manganese sulphate. They considered it to be due to a secondary action and proposed that the reaction in fact took place in two stages,²



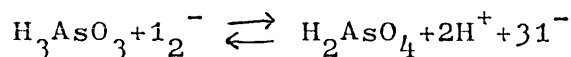
In their work, Guldberg and Waage also introduced the idea of reaction sequence. Their equilibrium reaction, however, stemmed from a totally different system, a heterogeneous one. It is almost certain that they did not realise the significance of their reaction integer in the stoichiometry of the chemical equation nor had they considered the complexity arising from different numbers of molecules taking part in the reaction.

The problem of deriving correct rate laws from equations representing chemical equilibrium has remained a subject of enormous difficulty and complexity. Roebuck, at the beginning of this century, showed that in the reaction of

1. J. W. Mellor, Op. cit., 96

2. Phil. Trans., 1866, 156, 201

arsenious acid with iodine, in the presence of iodide,



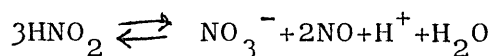
the forward reaction rate was proportional to

$$\frac{[\text{H}_3\text{AsO}_3][\text{I}_2]}{[\text{H}^+][\text{I}^-]^2}$$

and the reverse rate followed a dependency of

$$\frac{[\text{H}_2\text{AsO}_4][\text{H}^+][\text{I}^-]^2}{[\text{H}_3\text{AsO}_3]} \quad 1$$

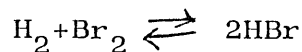
The complexities of ionized reactions were particularly evident and many were not studied until the early decades of the present century. They confirmed that the simple 'law of mass action' (LMA) could not be interpreted literally in a great number of cases. Abel et al. studied the decomposition of nitrous acid



According to LMA, the forward rate would be proportional to $[\text{HNO}_2]^3$. They discovered that, in fact, the rate is proportional to $[\text{HNO}_2]^4$ and inversely proportional to $[\text{NO}]^2$. The rate of the reverse reaction was proportional to

$$\frac{[\text{HNO}_2][\text{NO}_3^-][\text{H}^+]}{[\text{NO}]^2} \quad 2$$

Amongst the first gas-phase reactions to be thoroughly studied kinetically were the reactions between hydrogen and the halogens. Bodenstein and Lind showed empirically that in the formation of hydrogen bromide from hydrogen and bromine,



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1. J. Phys. Chem. 1902, 6, 365; 1905, 9, 727
 2. Z. Physik. Chem., 1928, 134, 279;

the rate of the forward reaction is of the form

$$\frac{[\text{H}_2][\text{Br}_2]^{3/2}}{[\text{Br}_2] + [\text{HBr}]} \quad 1$$

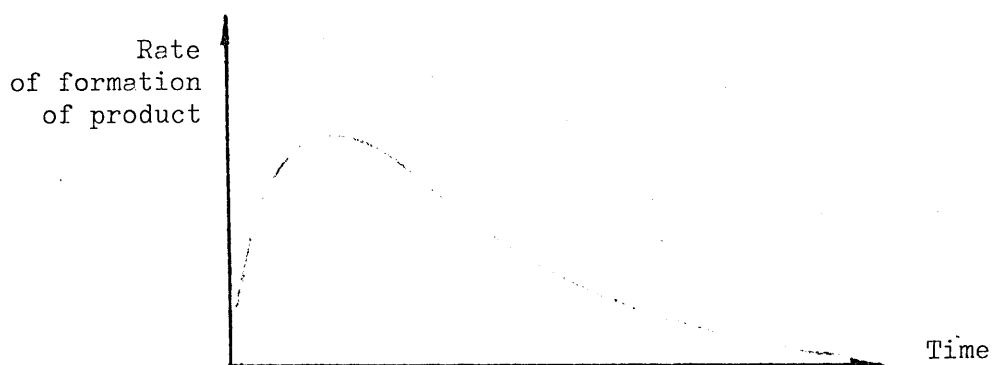
Thus, under experimental conditions, it was shown that, far from obeying a simple mass law, the reaction velocity of the forward phase decreases with increasing concentration of HBr to a certain limit. But it is the ratio of hydrogen bromide and bromine concentrations which determines the velocity, and not, as would be expected from the law of mass action, the absolute concentration of merely the hydrogen bromide. Just over ten years later, Christiansen, using Bodenstein and Lind's data was able to establish the mechanism for the hydrogen, bromine reaction.²

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1. Z. Physik Chem., 1907, 57, 168
 2. Det. Kgl. Danske Vibenskabnes Selskab. Mathematisk-fysiske Meddelelser, 1919, 1, 14 (in English)

2.5.3. An Exceedingly Curious Phenomenon: The Period of Induction.

The increasing number of studies on chemical reaction rates during the middle and latter half of the 19th century quickly led to a number of anomalous discoveries which delineated the role of time. One of the first problems encountered by the pioneers of rate studies related to changes at the very beginning of chemical reaction, the phase which van't Hoff, in his study of chemical dynamics, called "an exceedingly curious phenomenon."¹

In a simple reaction, of the type $A \rightarrow M$, $M \rightarrow B$ where M is some intermediate stage, it was very early on observed that there existed a well-defined period of acceleration, during which the velocity of reaction gradually increases to a maximum. This increase is followed by the usual curve of diminishing velocity, characteristic of chemical reactions in general. This reaction curve is also interesting from



another point of view. Since the curve approaches the time axis asymptotically, the reaction, theoretically speaking, can only end when time approaches infinity. Earlier, Mills, intent on demonstrating the principle of continuity in

1. J.H. Van't Hoff: Op.cit., 91.

chemical change, remarked:

the process of exhaustion of the chemical energy of a substance requires an infinitely great period of time for its accomplishment.¹

On this basis, he concluded that,

we can understand how a chemical reaction is possible. It can begin because it has never ended..... every substance retains a minute but real reserve of unexhausted energy.²

The existence of such an anomalous period at the start of chemical reactions had been recognised since the beginning of the 19th century, on an experimental basis. In 1801, William Cruickshank reported, in Nicholson's Journal, some experiments involving the action of chlorine on hydrogen and other gases. He recorded:

If the pure oxygenated muriatic acid, in the form of a gas, be mixed in certain proportions with any of these inflammable gases and introduced into a bottle filled with and inverted over water, though no immediate action may be at first perceptible, yet, in twenty-four hours a complete decomposition will be found to have taken place, the products varying according to the nature of the gases employed....³

Cruickshank was probably the first to record the phenomena of this time lag at the beginning of chemical reactions.⁴ The

1. E.J.Mills, Phil.Mag, 1876, 1, 1.

2. ibid.

3. W.Cruickshank, Nicholson's Journal, 1801, 5, 202.

4. J.W.Mellor, J.Chem.Soc. 1901, 79, 216.

explosive combination of hydrogen and chlorine mixtures when exposed to direct sunlight was also studied by Gay-Lussac and Thenard in 1809¹; the properties of the same mixture appear to have been studied continuously in a series of investigations from that time onwards. Dalton, for instance, repeated Cruickshank's experiments observing that:

the gases, after being put together (over water) seemed to have no effect for one or two minutes, when suddenly the mixture began to diminish with rapidity.²

Seebeck, writing to Göeth in 1810, intimated the role of light in the combination of these two gases; a mixture of hydrogen and chlorine contained in a clear glass vessel detonated in sunshine, whilst under a dark blue glass, combination occurred without explosion in one minute, and under a dark red glass the action took place very slowly or not at all.³

Bunsen and Roscoe, in a series of now famous experiments, first used the expression 'period of photochemical induction' to describe the phenomenon of delayed interaction for reactions which were induced by exposure to light. They observed in an experiment, in which chlorine and hydrogen were exposed to light, that during the period of acceleration, the quantity of change which occurred in the eighth minute

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1. Alembic Club Reprints, No.13, 43.
 2. J.Dalton; A New System of Chemical Philosophy, Manchester 1810, 2, 360.
 3. quoted in J.W. Mellor, J.Chem.Soc. 1901, 79, 216.

was ten times that which occurred in the first.¹ A similar phase was also discovered in the reaction between bromine and tartaric acid, in the absence of light. Bunsen and Roscoe named this general phenomenon "chemical induction". Initially, they had considered a sufficient explanation of the acceleration period, observed in the action of light on mixtures of chlorine and hydrogen, as being due to movement of molecules. Thus, the light which is absorbed by the mixture of chlorine and hydrogen induces a dislocation of molecules and this must reach a certain magnitude before the reaction can proceed. (Budde also thought that light acted on the chlorine/hydrogen mixture, by loosening the bonds joining the atoms in the molecules.³) However, Bunsen and Roscoe abandoned their ideas on the role of light, after their bromine/tartaric acid experiment,² which did not require the presence of light, concluding

The occurrence of such a maximum appears, therefore, to depend, not on some special peculiarity in the

1. R.Bunsen, H.E.Roscoe, Pogg. Ann. 1855, 96, 373; Phil. Trans. 1857, 146, 355, 601.

2. Actually, as Mellor pointed out, the tartaric acid experiment did not disprove their "dislocation hypothesis", since there was the possibility that the mechanism for the union of hydrogen and chlorine in light may be different from other reactions taking place in darkness. (J.W.Mellor, op.cit. p.117). Other work at the time indicated perhaps that the 'dislocation' theory could be revived with some modifications.

3. E.Budde, J.prakt.Chem., 1871, 2, 4, 431; 1873, 7, 376.

action of light, but on the mode of action of the force of affinity itself.¹

In 1862, Berthelot and Péan de Saint-Gilles recorded similar observations during their etherification experiments, which they called the period of "initial acceleration". This phenomenon, they thought, was of specific character, due perhaps to some sort of inherent resistance which had first to be overcome:

Pour concevoir l'accélération initiale il faut admettre une sorte d'inertie, de résistance à vaincre qui retarde la combinaison dans les premiers instants.²

The phenomenon of chemical induction and initial acceleration appeared increasingly frequently in chemical literature in the decades that followed, without any satisfactory theory being realised³. Evidence of the phenomenon also extended gradually into other types of chemical reactions, both homogenous and heterogeneous. Thus, Wright and his collaborators studying the reduction of metallic oxides by hydrogen and carbon monoxide in 1879 observed:

1. R. Bunsen, H.E. Roscoe, op.cit.

2. M. Berthelot, P. de Saint-Gilles, Ann.Chim.Phys. 1862, 3, 66, 26.

3. The reaction between H_2/Cl_2 was of special interest and investigated by Mellor, (following the work of Draper in 1843), Bunsen & Roscoe, (described above), Bevan in 1903, Burgess & Chapman, in 1904: see J.W. Mellor, Chemical Statics and Dynamics, London, 1904, 414.

In all cases, for a length of time the action is so slight as to be almost or quite imperceptible, after which it goes on at an accelerating rate until a maximum rate is attained, when it again diminished it is evidently a case of the chemical induction studied by Bunsen and Roscoe.¹

This time lag at the beginning of chemical reactions, or period of induction, was distinguished by the occurrence of two distinct phases; an initial period of inertness during which no observable chemical reaction occurred, followed by a second phase of increasing rate of chemical transformation.² Experimental evidence which was gradually accumulating showed that the two phases varied enormously in length. For hydrogen and chlorine, combining under the influence of light, the period of inertness was found to be so short as to be almost non-existent.

The theoretical importance of this unexplained time factor at the beginning of chemical reactions could not be doubted. If the sequence of events which characterised a reaction was to be fully understood, it was imperative to understand this phenomenon at the start of a reaction. Added to this, mounting experimental evidence pointed to the period of induction as a characteristic feature of all chemical change. Van't Hoff, in 1884, observed that this initial acceleration period was incompatible with the theory of

1. C.R.A.Wright, A.P.Luff, H.Runie, J.Chem.Soc., 1879, 35, 475.

2. E.J.Mills, W.McD.Mackay, Phil.Mag., 1883, 5, 16, 429;

V.H. Veley, *ibid*, 1894, 5, 39, 165.

chemical rates and in particular would violate the law of mass action.¹ Quoting the work of Urech, who had found the same phenomenon in the case of reactions between bromine and fatty acids, van't Hoff pointed out:

These results would be incomprehensible from a theoretical point of view, if the action of the bromine consisted of a simple substitution, for then the maximum velocity must occur at the beginning of the reaction.²

The cause of this phenomenon was considered by van't Hoff to be due to disturbing actions in the course of a chemical change.³ In his Studies in Chemical Dynamics, he had devoted one of the earlier chapters to a discussion of disturbing actions or secondary actions in the course of chemical change.⁴ Neglecting the obvious irregularities such as lack of homogeneity of reactants, evolution of heat during the reaction, and the occurrence of secondary transformations, van't Hoff described the major cause of irregularity in homogeneous reactions as being due to the influence of the medium.⁵ Under this influence, the data relating to the reaction would not be comparable with each other in the different periods of its course, because the

1. J.H. Van't Hoff, Studies in Chemical Dynamics, London,

1896, trans.T.Ewan, 91.

2. J.H.Van't Hoff, op.cit., 94.

3. J.H.Van't Hoff, op.cit., 91.

4. J.H.Van't Hoff, op.cit. ,26.

5. ibid. ,27

medium is gradually modified as a consequence of the accumulation of the products of the reaction. Experimentally, the influence of the relative quantities of the reactants or medium on the velocity of chemical reaction had been well demonstrated in almost every investigation involving rates of change. Berthelot and St. Gilles showed that an excess of alcohol retards the etherification of acetic acid to such an extent that a gram molecule of the latter was transformed in 4 hours at 100° .¹ The subject was later investigated very thoroughly by Menshutkin in a series of papers.² Thus in the combination of triethylamine and ethyliodide, the velocity of reaction is over 700 faster using benzyl alcohol as solvent compared with hexane as solvent; an excess of aniline was found to retard its own reaction with acetic acid. Similarly, Meyer reported that the velocity of nitration of benzene increases proportionately to the square of the quantity of nitric acid used, whilst the same reaction is diminished by excess of benzene.³ The influence of the medium or other foreign substance was thus considered by van't Hoff to be sufficient to explain many of the anomalous velocity changes during chemical reactions in solution.⁴ Van't Hoff also investigated three other experiments: the 'monosymmetric sulphur' produced during the transformation of rhombic sulphur into the mono-symmetric form was found to accelerate

1. M. Berthelot, P. Péan de St-Gilles, Ann. Chim. Phys., 1862, 3, 66, 90.

2. N. Menshutkin, Berichte, 1882, 15, 1618; Zeit. phys. chem., 1887, 1, 627; 1890, 6, 41.

3. L. Meyer, Zeit. Phys. Chem., 1888, 2, 713; Berichte, 1889, 22, 18.

4. J. H. Van't Hoff; op. cit., 29.

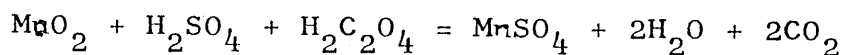
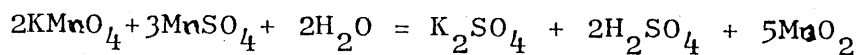
the change¹; during the electrolytic transformation of hydrogen and oxygen into water at 440°, there is a well-defined period of acceleration in the presence of nitrogen. In the absence of nitrogen, there is no acceleration. Van't Hoff thus concluded that the initial increase in velocity was due to the formation of nitrogen oxides, formed as a result of the electric discharge; the polymerisation of cyanic acid into 'cyamelide' is accompanied by an initial acceleration, due to the cyamelide. The acceleration was also conditioned by changes in the walls of the vessel.²

In all the cases considered, van't Hoff referred to the cause of the period of induction as 'secondary actions'. The possibility of these secondary actions as being due to catalytic agents is not mentioned, although he had earlier established the catalytic effect of aqueous vapour in the formation of ammonium carbamate.³

By 1902, Mellor had established that the period of induction is characteristic of chemical reactions which take place in a series of intermediate stages.⁴ This was evident from the studies of Harcourt and Esson on permanganate and oxalate.⁵ As we have already seen, Harcourt considered the existences of consecutive reactions very early on in their rate studies. They observed an initial acceleration

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1. J.H.Van't Hoff; op.cit. ,94; the results were those of T.A.Reicher: Inaugural Dissert, Amsterdam, 1883, 45.
 2. J.H.Van't Hoff; op.cit. ,97.
 3. ibid., p.34.
 4. J.W.Mellor, J.Chem.Soc., 1902, 81, 1280.
 5. A.Vernon Harcourt and W.Esson, Phil.Trans., 1866, 156, 193, 201.

of the reaction between potassium permanganate and oxalic acid in the presence of sulphuric acid and manganese sulphate. The reaction took place in two stages



The second reaction is the one actually observed and which exhibits the acceleration, due to the formation of an intermediate stage of oxidation of manganese to an oxide.¹ Thus the period of induction occurred because,

chemical change consists in the gradual formation of a substance which at the same time slowly disappears by reason of its reaction with a proportional quantity of a third substance.²

It was now possible to distinguish various origins for the general cause of this initial period of acceleration at the beginning of chemical reactions. It was observed for reactions which took place in several consecutive stages; a slowly progressing reaction could be accelerated by the presence of products, as a result of a side reaction or of the main reaction, as in catalytic agents. The acceleration was the direct result of the overcoming of passive resistance, the theory proposed initially by Berthelot. This idea was later revived because several experiments indicated that chemical reactions which took place imperceptibly slowly at one temperature may proceed with enormous speed at another. This has been briefly discussed in the previous

1. Phil. Trans., 1866, 156, 193, 201

2. ibid.

section on the effects of temperature and time.

In retrospect, the problem of the period of induction had not been resolved in any general sense. Rather, its existence emphasised that the stages by which chemical changes occurred were made up of complex steps, each of which required careful study to achieve total understanding. The initial acceleration complicated time factors at the beginning of a reaction; the order and molecularity dictated the velocity with which the reaction would proceed; and the law of mass action indicated the reaction conditions at equilibrium. The nature of chemical studies, as the years of the 19th century drew to a close, shows clearly that more and more chemists were closely examining each individual reaction on its own merit and providing the answers to how and why reactions occurred, in the form of reaction mechanisms. In all aspects of this new chemical discipline, the importance of time factors had been fully established.

Part 3

3.1. Time, Chemistry and Philosophy

3.1.1. Chemists and Time

The incorporation of time elements into chemical thinking was not, of course, limited to the work of the few chemists we have discussed. Reference to the role of time in chemistry generally, and the speed of reaction in particular, are to be found in many other well known writings of the 19th century.

The time factor necessary in the conversion of living tissues into non-living substances had been considered by Justus von Liebig in his influential Animal Chemistry of 1842.¹ Liebig summarized his findings in a series of hypotheses on the phenomena of motion in the animal organism. In a given time, only a limited amount of mechanical force can be manifested, and only a limited amount of heat can be liberated:

"That which is expended, in mechanical effects, in the shape of velocity, is lost in time.

The sum of the mechanical force produced in a given time is equal to the sum of force necessary, during the same time, to produce the voluntary and involuntary motions. The amount of living matter, which in the body loses the condition

1. J. von Liebig, Animal Chemistry, 1842; New Edition with notes by F. L. Holmes, New York, 1964.

of life, is, in equal temperatures, directly proportional to the mechanical effects produced in a given time. The amount of tissue metamorphosed in a given time may be measured by the quantity of nitrogen in the urine."¹

Liebig, by relating the actions necessary to convert living tissues into "lifeless compounds" as a function of the rate of mechanical output was, effectively, applying kinetics to biological systems. His work on animal chemistry, thus, anticipates the kinetic studies of Guldberg/Waage and Harcourt/Esson by several decades. The results, however, were expressed² in a notably qualitative rather than quantitative manner.

The analogy between biological and mechanical systems recalls the methods adopted by the two later teams, in establishing a familiar model on which to base their chemical systems.

Guldberg and Waage's chemical equilibrium was not unlike Liebig's idea of biological equilibrium: "That condition of the body which is called health includes the conception of an equilibrium among all the causes of waste and of supply; and thus animal life is recognised as the mutual action of both; and appear as an alternating destruction and restoration of the state of equilibrium".³

Liebig also equated the time required for sleep, during which the human body, with sufficient food, recovers its

1. J. von Liebig, op. cit., 233.

2. The application of kinetics to biological systems was later studied by Arrhenius; S. Arrhenius, Quantitative Laws in Biological Chemistry, London, 1915.

3. J. von Liebig, Animal Chemistry, op.cit. ,233-4.

losses, to the total force expended in waking hours. The mass of the body, too, was related directly to the rate of expanded motion by bodily functions.¹ In effect, Liebig had formed the basis of a kinetic theory for biological systems which used mechanical output as a function of chemical changes.

In fact, Liebig also carried out a number of careful studies into the effects of time on chemical change. In a paper published in 1848 entitled "On the Influence of Time on the Formulation of chemical compounds," he had called attention to the conversion of a concentrated solution of oxalic acid in alcohol into oxalic "ether" and oxalovinic acid, when kept at a temperature of 40° to 50°C, for several months.² Liebig discovered that not all acids, in contact with alcohol under the same conditions, change into an ether, first requiring the action of a 'mediating' agent. Benzoic acid, for instance, could be left in warm alcohol for weeks without effect; if, however a few drops of hydrochloric acid was added and the mixture left, while warm, for 8 to 14 days, the chlorine compounds first produced, succeed in bringing about the chemical change. Liebig considered that the formation of acetic ether in stored wines was probably due to the same cause.³

Even earlier, Liebig, together with Friedrich Wöhler, had observed that in the transformation of ammonium cyanate

1. J. von. Liebig, op. cit., 239

2. J. von Liebig, Ann. der Chem. und Pharm., 1848, 65 350.

3. ibid.

into urea, the change takes place immediately on boiling the aqueous cyanate solution, but was only gradual when the solution was left to evaporate in the air or by application of gentle heat.¹ It was to be over half a century later before Walker and Hambly applied the newly established theories of chemical kinetics, to the same problem, in a quantitative analysis which pointed the way to a mechanistic explanation.²

Liebig would undoubtedly have accepted this sequence of developments philosophically. "No subsequently developed idea can precede in order of time an earlier one -- with the earlier idea, the development of all subsequent ones is bound up" he wrote, towards the end of his exceptionally productive life.³ His philosophy, indeed, appeared to be that of temporal order, assuming that: chemical analysis resulted from the manipulation of the metallurgists; mineral chemistry from pharmacy and from chemico-technical manufacturers; and that organic chemistry was the child of medicine.⁴ Liebig's comment, that the factor of time was nothing but the sequence of chemical reactions, which awaited explanations, proved to be a prophetic one.⁵

1. Ann. Phys. Chem., 1830, 20, 393.

2. J. Walker, F.J. Hambly, Trans.Chem.Soc., 1895, 67, 746.

3. "On the Development of Ideas in Natural Philosophy."
Chem News, 1867, 252.

4. ibid., 263

5. Ann.Chem et Pharm., 1850, 75, 115.

Experimentally, Marcellin Berthelot and Péan St.Gilles, had been among the first to recognise the importance of timed reactions, and their work was to be the precursor of Guldberg and Waage's investigations into mass action.¹

Writing in his Essai de Mécanique Chimique, published in 1879, Berthelot remarked "---- dans la plupart des cas, les réactions ne sont pas instantanées. Le temps est donc nécessaire pour l'accomplissement des réactions chimiques, de même que pour tous les autres phénomènes mécaniques."²

He continued:

le rôle du temps a été pendant longtemps négligé en chimie, --- on peut même dire que jusqu'à les travaux sur la synthèse des corps gras neutres (1854), l'importance théorique du temps en mécanique chimique était à peu près méconnue."³

Berthelot believed that he and St. Gilles were the first to carry out systematic studies of time effects in chemical reactions. This, of course, entirely neglects the earlier contribution of Wilhelmy. However, Berthelot does discuss the importance of temperature in controlling the speed of reaction in both the homogeneous and gaseous states. Curiously, already well into the second half of the 19th century, when considerable chemical data was accumulating in the area of rate studies, Berthelot's writing did not mention

1. M. Berthelot, Essai de Mécanique Chimique, Paris, 1879.

2. ibid., 13.

3. ibid., 14.

the major progress made since the time of his own work.

As a permanent secretary of the French Academy of Sciences and Professor of Chemistry at the Collège de France, Berthelot was undoubtedly aware of the scientific progress being made during his own lifetime, and in chemistry especially. Speaking at a dinner held in 1894, Berthelot outlined his dream of a chemical future, in the year 2000.¹ By this time, he thought it probable that chemical energy (thermal and solar) would have resolved all energy problems. The production of foodstuffs, also a chemical problem, would have been overcome, by the abundant availability of this chemical energy. For nourishment, humans would "carry around with him little nitrogen lozenge, his little pot of fats, his little piece of sugar, his little flagon of aromatic spices, adapted to his personal taste." ²

Freed by advanced chemical and technical knowledge from the effects of the four seasons, all food problems resolved, "Man will gain in kindness and in morality, because his means of existence will no longer be dependent on the slaughter and destruction of living creatures." True to a 'modern' alchemical image, Berthelot considered "what vegetables have done to date with the help of energy derived from their surroundings we are already achieving, and we shall achieve it far better, more extensively and to greater perfection than does Nature, for such is the power of synthesis." ³

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1. M. Berthelot, In the year 2000, speech given before the French Chemical Products Ass., 1894, translated by A.A.E.E. Ettinghausen, Chem. in Brit., 1979, No.5. May, 250.
 2. ibid.
 3. M. Berthelot, op.cit.

Even more amazing, this radical revolution, brought about by the power of chemistry, would enable us "to realise the dreams of socialism, provided that we have succeeded in discovering a spiritual chemistry which is able to change the ethical nature of man as profoundly as our chemistry is transforming material nature."¹

So near now to the time set by Berthelot for the realisation of his dreams, the realities of chemistry and its relation to world development need hardly be commented upon here! In any case, it is doubtful whether Berthelot's world, dominated by chemical synthesis, in which "there will no longer be fields laden with crops, nor vineyards, nor meadows full of cattles" would necessarily have gained much enthusiastic support for chemistry.

Undoubtedly, it was a time when it would have been safer for chemists to be engaged in retrospection, than to be making auguries. Ostwald, writing in 1909, recounted the contributions to studies of time in chemistry to include the early work of Wenzel, who measured the rates of dissolution of different metals in acid, in an attempt to study affinity forces.² The long interlude between this first chemical rate investigation and further work on temporal effects in chemistry was broken only by Berthollet's 'Statique Chimique'. Ostwald considered Berthollet's rate studies, relating to heat dissipation, to be an isolated case and of purely

1. M. Berthelot, op. cit.

2. W. Ostwald L'Evolution d'une Science, La Chimie, Paris. 1909, 252.

theoretical nature.¹ Actually, Berthollet had also made time observations relating to affinity studies in his work of 1801.²

But Ostwald quite rightly observes that the specific study of the speed of chemical reaction was to re-emerge only half a century later, in the work of Ludwig Wilhelmy. It is probable that Wilhelmy's pioneering rate studies would have passed unnoticed but for Ostwald's timely intervention. Wilhelmy's contribution to rate studies is considerable, as Ostwald pointed out, since the concept of chemical speed of reaction had not, up 'til that time, being formulated. Why had the simple principle discovered by Wilhelmy taken so long to emerge? Ostwald blamed the long interval which separated the work of Wenzel and Wilhelmy on the fact that chemists were totally preoccupied with other problems.

This 1909 publication is particularly interesting because it contains one of the earliest historical account of the development of rate studies in chemistry. It includes brief discussions of the results of Berthelot and Péan St.Gilles, Harcourt, Esson, Guldberg and Waage and Von't Hoff. Ostwald considered that all were working independently of each other, but all obtained the same result. In fact, as we have seen, although the combined work of these chemists did indeed establish the subject of chemical dynamics as an independent discipline, their approach and method of analysis were notably

1. W. Ostwald, op.cit., 253.

2. C.L.Berthollet, Récherches sur les Lois de l'Affinité, Paris, 1801.

different. To Harcourt and Esson, Ostwald attributed the discovery of the principle that in a complex sequence of reactions, each step of the reaction acts as if it were alone. To Guldberg and Waage is attributed the discovery of chemical equilibrium as the result of two opposing reactions.

In this same work, Ostwald enunciated the statement with which he is most often associated in chemical dynamics: that at equilibrium, "on a affaire à un état indépendant du temps, l'équilibre chimique est un équilibre dynamique, ce n'est pas un équilibre statique". Earlier, Ostwald, giving the Faraday lecture at the Royal Institution, expressed his views on chemical progress strongly, with the words:

What are the most important achievements of the chemistry of our day? I do not hesitate to answer: chemical dynamics or the theory of the progress of chemical reaction and the theory of chemical equilibrium.²

He believed that it was possible to deduce from the principles of chemical dynamics all the stoichiometrical laws, the law of constant proportions, the law of multiple proportions, and the law of combining weights; there was no need for an atomic hypothesis. Ostwald's anti-atomistic

1. W. Ostwald, op.cit., 266.

2. W. Ostwald, The Faraday Lecture, J. Chem.Soc., 1904, 85, 500.

stand was not to survive the test of time.¹ However, his statement that chemical equilibrium denoted a state independent of time was to have longer, lasting, consequences, as we shall see in a later section. It continued to give credence to the general view that chemical phenomena largely embodied a static, timeless form of change. A closer examination of his original statement, however, shows that the ideas expressed may be interpreted differently and perhaps needed qualification. In Ostwald's words:

In its original meaning, this word (equilibrium) expresses the state of a balance when two loads are of the same weight. Later, the conception was transferred to forces of all kinds, and designates the state when the forces neutralise one another in such a way that no motion occurs. As the result of the so-called chemical forces does not show itself as a motion, the use of the word has to be extended still further to mean that no variation occurs in the properties of the system. In its most general sense, equilibrium denotes a state independent of time.²

Ostwald is here identifying with the classical concept of time as delineating motion: if there is no motion, there can be no time. In an absolute sense however, the statement is not truly viable. If, in a given state, action and

1. For an interesting account of Ostwald's anti-atomistic views, see D. M. Knight, "Steps Towards a Dynamical Chemistry", Ambix, 1967, 14, 179-197.

2. W. Ostwald, The Faraday Lecture, op.cit., 509.

reaction are equal and opposite, it would not be correct to say that no action or reaction (both motions) was taking place, only that their resultant is apparently static. Hence, the problem may be reduced to that of the familiar philosophical question of whether time is capable of an independent existence, an "absolute" time, independent of motion. However, even at a chemical level, Ostwald's statement can be called into question. For, as Williamson had clearly established: in statics, the phenomenon considered is one in a state of rest, whilst dynamics is concerned with its change.¹ The transition from the statical to the dynamical point of view consists of adding the element of time.² Since chemical equilibrium denotes, in Ostwald's words, a dynamic state, not a static one, it appears somewhat contradictory to dismiss the time factor, which distinguishes the two states.

Whatever the logic behind Ostwald's deduction, its influence has been considerable. Chemical equilibrium was a complex and elusive phenomenon for chemists to grasp in the 19th century and remained so for a long time afterwards. Possibly, Ostwald had not intended any philosophical reference to the concept of reversibility and directional time. But certainly, his ideas were to add to the philosopher's picture of the chemist's unspoken desire to "eliminate" time, as we shall see.³

1. A.W. Williamson, Notices of the Proceedings at Meet. of Memb. of Roy. Inst., 1851-4, 1, 90; see this work on Matter, Motion, Change and Continuity.

2. ibid.

3. This work, The Elimination of Time.

3.1.2. Chemists and Philosophy.

Among the diversity of chemical literature, there can also be found other examples of early consideration of the time factor in chemical processes which have not been touched upon in the present work.¹ Philosophically, too, the concept of time must have touched upon the lives and thoughts of not a few chemists, whose daily work called for the minutest observation of phenomenological change. It is a pity that so few took the time or leisure to record their thoughts for posterity. We learn, for instance, from Pearce Williams' study of Michael Faraday that fundamental problems of philosophy occupied Faraday's thoughts from his very early years.²

And time was amongst those ideas which the young Faraday puzzled over.³ It seems probable that Faraday's ideas on time were influenced by those of Berkeley, for he wrote to his friend Abbott on the subject using very similar words.⁴ Berkeley believed that "time is the train of ideas succeeding each other" and "duration cannot be distinguished from existence."⁵ This idea of time as a relative entity,

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1. see examples listed by E. Farber, Chymia, 1961, 7, 135.
 2. L. Pearce Williams, Michael Faraday, London, 1965, 80.
 3. Faraday's biographer appears surprised that the concept of time "even occurred to him". This in itself is puzzling, since undeniably time forms one of the fundamental problems of philosophy.
 4. ibid., 81.
 5. G. Berkeley, 1685-1753; Common Place Book, Vol.1, 58, Berkeley's Works, Ed. by J. Fraser, Oxford, 1901.

as opposed to Newton's theory of absolute time, was, in Pearce Williams' view, to have considerable influence on the development of Faraday's mature thoughts.

"In his view, time was equated with a succession of physical events, hence any phenomenon which endured in time necessarily implied a physical process. His efforts to detect the propagation of electric, magnetic and gravitational fields in time were inspired by this concept, for if such a time relation could be found, it would provide strong evidence for his view of the progressive transmission of force through space." ¹

It is, however, to Faraday's early mentor, Humphry Davy, that the most eloquent disquisition on time by a chemist must be attributed. His Consolations in Travel, written during extended travels in Europe whilst trying to regain health, lingers painfully on the over-riding emphasis of time as the originator of death and decay.² Knowing now as we do, from the many published studies of his life, the reasons behind Davy's thoughts, the work takes on a greater air of pathos. As the title suggests, Consolations was written as a self-consoling eulogy, a lament for opportunities lost, and an unregainable past.

In the last chapter of this work, entitled Pola or Time, Davy takes on the character of Philalethes who describes time

1. L. Pearce Williams, op. cit., 81.

2. H. Davy, Consolations in Travel or The Last Days of a Philosopher, London, 1830.

as the destroyer of all material forms:¹ But, asks Philalethes, do these destructions, innately chemical in nature, obey physical laws? To command Nature is but to obey Nature's laws, and these ravages of time are, at one and the same time, the creators of life as well as the cause of destruction.² Without change, which is the manifestation of time, there could be no life; without decay, there can be no rebirth. Changes which are continuously produced on earth, such as precipitation and other climatic factors, are the results of gravitation. Only bodies which can resist gravitation by the attraction of cohesion or by chemical attraction can be preserved - temporarily at least.³

Attraction, of whatever kind, results in rest, a sort of eternal sleep. This cohesion is ultimately destroyed by a conglomeration of factors; exposure to heat and cold, expansion, contraction, all changes of form which eventually bring destruction and decay. The causes of change, Davy thought, could be divided into mechanical and chemical. It is the chemical properties of effects such as electricity, which, though extremely slow and gradual, are none-the-less, the most effective in the great work of destruction.⁴ Whilst chemical change is a function of temperature, the solvent powers of water and the corrosion of metals are all made, poetically, qualities of time.

1. H. Davy, op.cit., 242.

2. ibid., p.242.

3. Consolations, op.cit., 243, 244.

4. ibid., 248

Davy's experiences, on his travels, afforded plentiful opportunities of witnessing examples of these chemical attributes of time, such as the leaning Tower of Pisa, whose granite was weathered and stained by the formation of iron oxides. Like time, oxygen, that great chemical agent, is at one and the same time, a necessity of all living processes and the bringer of all decay and destruction.¹

Together, the chemical agencies of water and air, assisted by those of electricity and gravitation, are sufficient to account for the merciless progress of time. The ravages on buildings afforded by these natural phenomena are further aided by the action of vegetation, animals and insects. "Add to these sure and slow operations, the devastations of war, the effects of the destructive zeal of bigotry, the predatory fury of barbarians seeking for concealed wealth under the foundations of buildings...and it is rather to be wondered, that any of the works of the great nations of antiquity are still in existence".²

Philosophically, Davy discerns a contradiction between the advantages of eternal preservation and the dynamics of change. To the suggestion that (supposing the constant existence of a highly civilized people) the ravages of time could be repaired, and by defending the finest works of art from the external atmosphere, their changes would be scarcely perceptible, his friend Eubathes replies that, perhaps, it was

1. H. Davy, op.cit., 253, 254.

2. Consolations, op. cit., 256.

not to the advantage of a people that its public works should be of an eternal kind. Left with no struggles or acts of creation for which to strive, inventive faculties would wither, as witnessed in history by the decline of the Roman Empire.¹

It is the relative quality possessed by time which endures, as Davy does not fail to point out. "Yet", says Eubathes, "when all is done that can be done, in the work of conservation, it is only producing a difference in the degree of duration,--- none of the works of a mortal being can be eternal, as none of the combinations of a limited intellect can be infinite. The operations of Nature, when slow, are no less sure; however man may for a time usurp dominion over her, she is certain of recovering her empire."²

Davy is here re-echoing the age-old dilemma of Man's struggle against nature, whilst purporting to obey its dictates. Mortals may create palaces, ships and houses from rocks, stones and trees, and mould metals with tools of water and fire. But with time, these works, no matter how perfect, begin to change and to decay. Temples, bridges, fortresses or even the splendid monuments raised to perpetuate the memory of Man's perishability are gradually destroyed by time. There can be no ultimate victory for humanity in a battle for domination against the forces of nature.

1. H. Davy, op.cit., 257.

2. Consolations, op.cit., 258, 259

Yet, says Philalathes, these changes of the material universe are in harmony with those which belong to the human body. Perhaps the unspoken law is that our material and tangible world bears the same relation to the divine and infinite Intelligence that our bodily organs bears to our mind. With the exception, that in changes of the divine system, there is no decay, since in the order of things there exists a perfect unity. Perhaps, in the last analysis, the principle of conservation is as eternal as that of¹ motion.

Hence, like van Helmont and countless others before him, the question of time, change and continuity become identified with a divine power, an omnipotent God. For surely, Davy thought, when-ever we attempt metaphysical speculations, "we must begin with a foundation of faith".² Time, Philalathes believes, is almost a human word, and change entirely a human idea. In the system of nature it is progress rather than change which we perceive.

To Davy then, though destruction is the chief attribute of time, yet it is not a static death but rather a dynamic rebirth. For though "the sun appears to sink in the ocean in darkness, it rises in another hemisphere". With Nature as ruler, that which is destroyed will, with certainty, live again in a period of succession.³ This dynamic view of time expressed by Davy in this, one of his last writings,

1. H. Davy, op.cit., 261.

2. Consolations, op.cit., 261.

3. ibid., 263.

is consistent with his earlier thoughts:

Change is the essence of all the operations of nature, and change may constantly be referred to motion. But for motion there must be a moving cause, and this necessarily implies the existence of active powers ... every species of attraction and repulsion that we are acquainted with may be the result of one grand and universally operating law. ¹

In his contemplations, Davy sees time as the link between history of civilization and the human search for chemical laws. His views appear, over a century later, as somewhat out-moded, with no insight into the far greater knowledge which time can bring. Few reflecting on the enigma of time now, as Davy was then, could credit such sentiments as he expressed, that "almost everything we have worthy of admiration is owing to what has been preserved from the Greek school; and the nations who have not possessed these works or models have made little or no progress towards perfection".²

Indeed, many of Davy's temporal ideas, which can be seen to merely echo the traditional philosophical schools of thought, appear far less profound than those of his protégé, Faraday. The thoughts of Newton, Leibniz and certainly

1. The Collected Works of Sir Humphry Davy, Ed. J. Davy, 1839-40, London, Vol. 8, 287-8.

2. Consolations, op.cit.

Berkeley appear not to have touched him even remotely. From the pen of one who had advanced the science of chemistry not inconsiderably, it is impossible not to feel a sense of disappointment at his reticence on the deeper significance of time. The thoughts that Davy laboured over were perhaps reflections of his own state of mind at that period, a time when he was seeking consolations rather than offering any scientific insights.

But the role of time in chemistry could indeed have been made more specific than that of a bringer of destruction, or even rebirth, as Davy intimated. Though clearly a factor present at the beginning and end of any phenomenon, its part in the sequence of changes was also vital and far more subtle. This role of time identifies the course of the change, in an anticipation of the end to which Davy so constantly referred. To use an euphemism, time permitted the chemist to travel hopefully rather than to arrive. And in order to prolong the travel, alchemists sought to eliminate the end or at least to extend it, as we shall now see. Davy, at the time, was clearly not travelling hopefully.

3.1.3. Time and Chemistry: the Elimination of Time.

The role of the chemical practitioner has always been associated with Nature, in a very special relationship. A role which, at times, appeared to be its helper and, at other times, its mortal enemy, in a constant battle for superiority. We have already seen how in the 19th century Berthelot's dream of a chemical future envisaged chemistry taking over nature's role and achieving even greater success. As Whitehead put it, "man, who at times, dreamt of himself as a little lower than the angel, has submitted to become the servant and the minister of nature it still remains to be seen whether the same actor can play both parts".¹

Alchemical art, at its simplest level, sought to achieve one aim: nature perfects metals in a thousand years; but, the alchemist asked, how can Man in his work of transmutation live a thousand years, seeing that a life could not be extended to even one hundred years? "What Nature cannot perfect in a very long space of time, that we complete in a short space by our artifice", said the alchemist, "for art can in many things supply the defect of Nature".²

But if this was the accepted role of the alchemist, a new awareness must soon have impinged on his consciousness; in his desire to become accomplished at competing with time, it must soon have become obvious that any discovery by

1. A.N.Whitehead, Science and the Modern World, London, 1938, 117.

2. From the Summer Perfectionist of Geber, see J. Read, Prelude to Chemistry, London, 1957, .49.

alchemy, even if supremely successful, was no match for the real thing. When Nature created gold, it lasted forever; gold was treasured for this property alone, its resilience to the ravages of time. Transmuted gold could not stand up to the test of time, or even the test of fire; it soon tarnished, and with it, the alchemist's reputation. And the most potent of elixirs only served to demonstrate, if he were lucky enough to survive its initial impact, that alchemical medicine was no challenge for eternity, for he soon needed another. The alchemist of old then, who sought to play the role of time, must have been more than aware of the fact that his existence was a temporary one, that he was bound by the same confines of time as those other mortals who did not play, literally, with fire. Perhaps more so.

The fact that alchemists and early chemists did not make any lasting attempt to incorporate this time element, which clearly pervaded even the simplest chemical operation, into their theory has encouraged the idea that chemists were, perhaps unconsciously, seeking to eliminate time from their philosophy. Thus Eliade has argued that in taking upon himself the responsibility of changing Nature, the alchemist put himself in the place of time.¹ His attempts to modify Matter, by inventing methods which would speed the transformation or transmutation of metals, from the aeons required by Nature, to that of weeks in the work-shop, made him a dictator of time. The dream was to be total master, to be able to extend

1. M. Eliade, The Forge and the Crucible, trans. by S. Corrigan, London, 1962, 169.

time into immortality; the ultimate desire of the early chemist was to change the laws limited by time.

And this tradition has passed down, according to Eliade's theory, into modern chemical thinking. 19th century chemical progress was no less imbued with this desire to supplant time than ancient alchemy. "We must not believe", wrote Eliade, "that the triumph of experimental science reduced to nought the dreams and ideals of the alchemist. On the contrary, the ideology of the new epochs, crystallized around the myth of infinite progress and boosted by the experimental sciences and the progress of industrialization, takes up and carries forward - despite its radical secularization - the millenary dream of the alchemist."¹ Paradoxically, Eliade identifies the 19th century, the very era in which time finally becomes incorporated formally into chemical thinking, as the age in which chemists at last succeeds in supplanting time: The discovery of synthetic methods in organic chemistry demonstrated the feasibility of eliminating time, preparing in factories and laboratories, substances which would have taken Nature far longer to produce - the ultimate *raison d'être* for the alchemist, perfected.

But in Eliade's mind, there is a fine point of distinction between the attitudes of alchemists and modern chemists, towards time. Although he put himself in the place of time, the alchemist took good care not to assume its roles.²

1. Eliade, op.cit. ,172.

2. ibid., 174.

His dream was to accelerate the tempo of things, to create gold more quickly than Nature. He refused to admit to himself that he was, essentially, a temporal being, contriving by every means to conceal from himself his vulnerability to the irreversibility of time. By contrast, modern man has taken on the role of time by accepting reality and recognizing his temporal being. Man can achieve things better and faster than Nature, if he submits his life to work. The work of time could be overcome by simply choosing the amount of time given to work. For Eliade, the temporality assumed and experienced by man is translated, on the philosophical plane, into the tragic awareness of the vanity of all human existence.¹

Although we may agree with much of Eliade's argument, his theories are, in a curious way, weakened by his belief that the alchemists were not all aware that their art did the work of time. And furthermore, Eliade considers this unimportant - the essential point is, he maintains, that their work involved, in one form or another, the elimination of time.² Actually, extant alchemical literature would suggest that alchemists were only too well aware of their role in the universal enigma of time.

Thus early analogies for alchemical processes included the creation of earth by God as given in the Book of Genesis, the passing of the four seasons and the process of creation

1. Eliade, op.cit. .177

2. ibid., 171.

in general.¹ Alchemists like Zosimos described the completion of their work with expressions such as "the time of gestation is not less than 9 months when there is no miscarriage"². Geber considered that in performing a transmutation, the chemist was merely carrying out in a short time what Nature performs in a long time.³ All those concerned with alchemy knew that successful chemical processes required time for completion:

I took natural quivering mercury, free from impurity, and placed it in a glass vessel shaped like an egg. This I put inside another vessel like a cooking pot, and set the whole apparatus over an extremely gentle fire. I heated the apparatus day and night for 40 days, after which I opened it. I found that the mercury had been completely converted into a red powder".⁴

Yet, though it was apparently recognised that time was a necessary element of chemical processes, the determinant nature of this time period remained obscure or 'divergent'. Thus Geber wrote, "the method can last as long as 70 years according to the variations the shortest method lasts 15 days. You see, dear brother, the divergence which these figures present: 70 years and 15 days".⁵

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1. See, for example M.P. Crosland, Historical Studies in the Language of Chemistry, London, 1962, 19.
 2. ibid., 20.
 3. The Works of Geber. Trans. by Richard Russell, 1678, a new edition with introduction by E.J. Holmyard, London and Toronto, 1928.
 4. Holmyard, op.cit., 26.
 5. M. Crosland, op.cit., 21.

The true significance and meaning of these temporal interludes remained open to interpretations, adding to the aura of alchemical mysticism. As Crosland puts it "it was always possible to say when a 'philosopher' spoke of a 'year' or a 'month' he meant a 'philosophical year', which was different from an ordinary year".¹ Those who considered these temporal discrepancies, in the writing of alchemists, worthy of interpretation sought for reconciliatory explanations.

"The philosophers have determined several periods of time for the preparation of our Art. Some have fixed this period at one year, others at one month, others again at 3 days and still others at a single day. But in the same way as we call a day the length of time taken by the sun to traverse the heavens from the east to the west, the sages have called a day the interval of time that elapses from the beginning of the cooking to the end. Those who speak of a month refer to the course of the sun through one sign of the Zodiac. Those who mention three days consider the beginning, the end and the middle of the work; and finally those who fix the time at a year, say this in respect of the four colours which form their four seasons".²

These brief descriptions of alchemical operations do imply a concern by alchemists for the element of time in their art and further more, it was the alchemists' prerogative to define this time, whether it be long or short.

1. M. Crosland, op.cit., 21.

2. quoted by Crosland, op.cit., 21.

What undoubtedly does distinguish later chemistry from earlier alchemical ideas was that, if mystical artifices permitted and encouraged obscurity in the form of allegories, chemistry, as a science, very clearly demanded something else - clarification and classification. It may be argued that the aims of modern science, as distinct from that in alchemy, seek to understand the phenomena of time. To formulate it, rather than to supplant it. Logic does not permit laws and theories to precede awareness and understanding. And is it possible after all to eliminate something which has not yet been formulated? This dilemma approaches the arguments put forward by Meyerson in his analysis of chemists and their desire to eliminate time.¹ Taking the behaviour of radioactive bodies as example, Meyerson considers the rate of decay of radium as a fundamental phenomenon in which the variation in time is entirely independent of every other circumstance.² The scientific law says that, "in 3.70 days the radio-activity of radium is reduced by one-half". In this case, a change in time can be expressed as a function of time.³ Throughout the change of the radio-active body, however, the one thing which has remained constant is the law according to which the change was produced, i.e. the relation between the change and time has remained true. So that, though "time, in its essence, flows always and uniformly in the same direction",

1. E. Meyerson, Identity and Reality, trans. by K. Loewenberg, London, 1929, 215.

2. Meyerson, op.cit., 220.

3. ibid

the relationship between time and the changing phenomenon has remained unaltered.¹

From a chemical point of view, this is particularly interesting, since chemistry is assuredly the study of phenomenological change. The role of law and theories in chemical change will be discussed in the last section of this work. The search for quantitative laws of chemical change by chemists like Peter Waage and Vernon Harcourt was essentially the search for the immutable relationship of which Meyerson talks. To him, the desire in science, by both observation and experiments, to uphold the conservation of "objects" in time, the "elimination of time formulae" is manifested most clearly in the development of chemistry.²

From the phlogiston theory, through the discoveries of Lavoisier, to the recognition of chemical equilibrium, the principle has remained the same; the desire to identify and equate the states representing the "before" and "after" of the change in time.³ This is, to Meyerson, the elimination of time. By identifying completely the antecedent and the consequent, everything has been preserved, everything has remained as it was - and time can be thought to have exercised no influence.

But, as Meyerson himself admits, this complete identification is, in reality, not possible. Clearly, within

1. Meyerson, op.cit., 220.

2. ibid., 222

3. Meyerson, op.cit., 222, 223.

the chemical system, somewhere between the 'antecedent' and the 'consequent', there has been a change, a displacement.¹ In Meyerson's day, however, he considered the nature of this displacement incapable of determination. "For if we wished to penetrate more deeply into the explanation of the phenomenon", wrote Meyerson, "to scrutinize its mechanism, we should be obliged to determine exactly the molecular motions - that is to commit ourselves upon the mode of displacement." This difficult task could be avoided, however, said Meyerson, by the simple fact that the explanation of chemical phenomena was still too little extended, "chemistry is not yet advanced enough to admit of true mechanical explanations".

Writing around the first decade of the present century, Meyerson was perhaps justified in many of his ideas on the state of chemistry. 'Mechanism', in chemistry, as we have seen in Part II of the present work, was a direct result of the study of the course of chemical change. This study, which first required the recognition, by chemists, of the dynamic aspect of their subject, was to lead to the establishment of chemical kinetics, a science still in its infancy in Meyerson's day.²

1. Meyerson, op.cit., 227.

2. Farrington Daniels, writing in 1938, referred to chemical kinetics as 'a recent development in chemistry and a difficult one'; Chemical Kinetics, Cornell Univ. Press, 1938.

Meyerson was a chemist. Born in 1859, in Lublin (Russian Poland), Meyerson was sent, while still very young, to Dresden and then to Leipzig and Berlin. On leaving school he studied chemistry, first at Göttingen, then at Heidelberg, under Bunsen. In 1882, he settled in France, where for some years he was engaged in business as a practical chemist.

Meyerson's argument then, is that science, in its effort to become "rational", tends more and more to suppress variation in time and that chemists are, above all, "guilty" of this. In developing his thesis, Meyerson has raised several interesting points. Firstly, in his analysis of science and the elimination of time, he has identified one very important element of scientific progress, the search for constants. This search was successful in physics long before it was in chemistry. But time is not, and cannot, always be eliminated in science. Maxwell's equations intimately involve time; so does thermodynamic irreversibility; so indeed does quantum mechanics, in which the effect cannot reproduce the cause.¹

Secondly, his idea that an understanding of "mechanism" was called for in order to identify more precisely the nature of displacement, and thus of time, in chemistry is particularly interesting in the light of the present work. Williamson as we have already seen, also identified this principle very clearly when he said that the transition in chemistry from the statical to the dynamical point of view, consisted in super-adding the consideration of time to that of space.²

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1. I should like to thank Dr. Robert Walgate for an interesting discussion on this aspect of Meyerson's ideas.
 2. Notices of the Proceedings at the Meetings of the Members of the Royal Inst., 1851-54, Vol 1, 90-94; see this work, Matter, Motion, Change and Continuity.

Thus it appears that the introduction of "mechanism", which Meyerson had considered chemistry as yet unable to achieve, did not "eliminate" time, but, on the contrary, "super-added" it to chemical phenomena. Williamson was, in fact, quite accurate in his belief. For the establishment of kinetics, which was to lead to an understanding of chemical mechanism, was to finally introduce time factors into the chemical equation.

From a present day vantage point, Meyerson's analysis is more applicable to classical science, and to classical physics in particular, than to modern concepts of scientific understanding. This is especially true in his definition of scientific laws and theories, as we shall discuss later. But Meyerson's personal approach to the philosophy of physics has had a profound influence on the thoughts of many later scientists, historians and philosophers of science.¹ It is perhaps regrettable that his only major reference to chemical phenomena conjured up a picture of something timeless and static. And particularly so, at a time when chemical dynamics was indeed becoming fully established as a new scientific discipline. It was picture however which chemists themselves, like Ostwald, had helped to create.²

1. Einstein, writing in The Times (February 5, 1929) referred to Meyerson's "brilliant studies in the theory of knowledge" as reflecting the same spirit of faith in the uniformity of nature and its accessibility to the speculative intellect as has inspired the work of the mathematician. See introduction by J.H.Muirhead to Meyerson's work, op.cit. More recently Kuhn has also written of his indebtedness to Meyerson's ideas: see T.S.Kuhn, The Structure of Scientific Revolution, Chicago, 1962.

2. See his statement on chemical equilibrium as a state "independent of time."

3.1.4 Chemistry and Philosophy

'The history of chemistry exhibits, in one respect, a remarkable parallel to the history of philosophy', wrote Edmund Mills in 1867; 'for no other sciences have transmitted to the present epoch so many unresolved and kindred controversies'.¹ The history of ideas concerning chemical phenomena is also very ancient. It comes as something of a surprise then to discover in a study of its history, however brief, that a philosophical basis for chemistry has not emerged in the process of its development. That this is the case, despite the fact that chemical principles are at least as old as those of physics, poses considerable reason for reflection.²

In the present work, a consideration of how time factors became established in chemistry has also involved a brief insight into how related epistemological factors had first to evolve: - the definition of chemistry, its quantification, and the concept of the course of chemical change were distinct stages of chemical development. These 'steps' in developing chemistry into an 'exact'

1. Phil. Mag., 1867, 37, 461.

2. On physics and philosophy, see: M. Cipek, The Philosophical Impact of Contemporary Physics, Princeton, 1961; P. Duhem, The Aim and Structure of Physical Theory, Trans. by P.P. Weiner, Princeton, 1954; H. Margenau, The Nature of Physical Reality, New York, 1950; P.W. Bridgman, The Logic of Modern Physics, New York, 1927; P. Frank, Modern Science and its Philosophy, Harvard Univ. Press, 1949; H. Poincaré, The Foundation of Science, New York, 1929; E.A. Burt, Metaphysical Foundations of Modern Physical Science, New York, 1925.

science has only occurred, relatively speaking, in recent times. Many revolutionary chemical ideas, such as those introduced by Wilhelmy, Berthollet, and Williamson were to lie dormant for many years before being re-vitalised. What would appear, in retrospect, as simple and logical steps in the development of human thoughts, were found, in reality, not to be so simple. Not infrequently, battles, albeit of a dialectical nature, had to be fought to overcome existing prejudices, contradictions, and confusions as to what chemistry was and was not; the battles were waged by post-renaissance figures like Paracelsus and van Helmont whose lives and work coincided with an era bridging the transition from alchemy to chemistry. They are remembered now as much for what they destroyed as created. The battles were also fought using the diadactic methods of Libavius and the later teachings of chemists like Harcourt who extolled the virtues of examining, not the products of chemistry, but the course of chemical change. These long struggles in the establishment of chemical thoughts have made the history of chemistry an immensely complex, and sometimes, an impossible story to follow.¹

The notion of belated developments in chemistry has been observed frequently by past historians. Butterfield's now familiar 'post-poned scientific revolution in chemistry' referred to the final triumphs of Lavoisier in the eighteenth century in making chemistry an 'exact science'.² But the

1. For an excellent account of the story, see R.P. Multhauf, The Origins of Chemistry, London, 1967.

2. H. Butterfield, The Origins of Modern Science, London, 1957

reasons as to why there were such post-ponements or delays appear, in retrospect, far more complex than Butterfield intimated. It is of interest therefore to reconsider a few of the chemical developments touched upon in the present work and to see how they may relate to philosophical considerations of the subject. Such developments include, for instance, temporal concepts, chemical dynamics, and the aims and structures of chemical laws and theories.

Ideas in philosophy are inextricably related to the intellectual realisation of the intangible, of which fundamental matter, time and space form the foundations. The infinite divisibility and, simultaneously, continuous nature of matter and time have posed familiar paradoxes to generations of thinkers in the development of science. Boscovitch, writing in the middle of the eighteenth century, pondered on questions in which we recognise an all too familiar echo: of worlds within worlds, and of our limited ability to experience them except as philosophical concepts, linking time and matter.¹ Was it not conceivable, wondered Boscovitch, that in some small grain of sand which we can hardly perceive, there is hidden a whole world in which there is an immense number of living beings? And was it not possible that there be a long series of such worlds, which, with respect to one another, would have the same relation as our single grain of sand has to the whole world? 'Whatever the truth of the matter'

1. R.J. Boscovitch, 'On the Relativity of Temporal Intervals', 1775; trans. in: 'Boston Studies in the Philosophies of Science', Vol. 22, Concepts of Space and Time, Ed. by M. Capek, Reidel, 1976, 225.

wrote Boscovitch,

What is for us a vanishing instant, seems to be a very long time to those very tiny living beings. In this respect, it occurs in those little animals (that is, those inhabiting the micro-world) something similar to what we observe in the pendulums of shorter lengths whose number of oscillations is in a given time so much larger, the shorter is their length. So these very tiny living beings, if they pass through three or four generations in a day regard this day as a century and two months would seem like a thousand years from the beginning of their world.¹

These reveries, akin to those we may all have had at one time or another, were not merely childish flights of fancy, but the thoughts of one whose atomic theory held enormous attraction and indeed had considerable influence on the minds of nineteenth century chemists, including Faraday.² As a philosopher, Boscovitch's ideas were intended to be reconciliatory, a wish perhaps to bridge the hiatus which separated the thoughts of Newton and

1. Boscovitch, op. cit.

2. L. Pearce Williams believes Boscovitch to have also influenced Davy and Dalton, but this is questionable; see Boscovitch and the British Chemists, in Boscovitch Studies, Ed. by L.L. Whyte, London 1961.

Leibniz.¹ For chemistry, Boscovitch believed optimistically that 'there can be found in this Theoria the general theory for all chemical operations'.²

(a) The Nature of Chemical Philosophy

Ideas of time, space, and matter were fundamental to the development of both physics and chemistry, a part of the inherited concept, as we have seen. If a reason for the lack of a concrete philosophy in chemistry is to be sought, clearly, it can not be found in the origins of matter or time theories, to which both sciences were heirs. More likely, it is to be found in an inherent difference of approach to the nature and purpose of the two sciences. It has frequently been remarked that chemistry, from its very beginnings, has followed an eminently practical path of development. The mystical arts of alchemy were ultimately aimed at seeking an extension of life, if not material wealth; several millenia later, the consequence of quantification of time in chemical processes was to make industrial production more efficient.

Recently, Theobald has suggested than an explanation

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1. See for example: A. Thackray, Atoms and Powers, Oxford, 1970, 151.
 2. His theory of matter reduced atoms to 'points', which involved only two explanatory categories, force (or length) and time. See Thackray, op.cit.

of the hiatus between chemistry and philosophy lies in the general concern of chemistry with things at what might be called an 'intermediate level of physical complexity'.¹

Because chemistry deals with molecules, rather than atoms, it deals with things supposedly less 'fundamental' than atoms.² On the other hand, it deals with things less 'complicated' than, and therefore more 'fundamental' than the genes, organisms, cells and species of the biological sciences.³ However, as Theobald himself points out, these terms, simple, complicated and fundamental are mere semantics, 'along a scale of esteem', with no particular relevance to the development of modern chemistry.

The roots of the problem, as Theobald sees it, relate more to a difference in temporal emphasis between chemistry and physics, as evidenced by many of the concepts commonly used by chemists.⁴ Theobald argues that terms

1. D.W. Theobald, Chem. Soc. Rev., 1976, 5, 203.

2. D.W. Theobald, op. cit., 204.

3. ibid.

4. ibid., 209

such as:

substance	equilibrium
molecule	bond
functional group	bond strength
reactivity	solvation
steric interaction	valency
stability	transition state
symmetry	

are static, organising and descriptive concepts,
more like concepts in biology than the causal
dynamic concepts of so much of physics.¹

and further more;

they are not vulnerable to vulgar resting,
for they are designed to make sense of large
and timeless ranges of experience rather than
to explain the particular individual cases.²

This idea, that the chemical terms listed, though
far from being exhaustive, all pertain to static,
timeless ranges of experience, is an interesting one.
It echoes the thought of Meyerson and Eliade, that
chemists and chemistry have frequently sought to
eliminate time from their substratum, the chemical
concepts themselves. Yet, strangely, it can be seen
from this list, that these chemical phenomena are all,
without exception, descriptive of active rather than
static states. Thus, reactivity, steric interaction,
solvation, and transition state all emphatically imply
activities which are, at the very least continuous, if
not ceaseless. The classifications functional group,

1. Theobald, op cit., 209.

2. ibid., 210.

symmetry, bond, valency denote states which are on the point of changing; at best static animation, since groups are only functional if something can be added or subtracted from it, symmetries are not permanent and bonds and valencies are descriptive of forces which serve to quieten potential chemical energy, and without which the picture is one, as of old, where atoms and molecules would fly apart. Even stability implies a state relative to another which is less stable, also embodying temporality.

Above all, equilibrium: 'l'équilibre chimique est un équilibre dynamique, ce n'est pas un équilibre statique', wrote Ostwald.¹ Yet paradoxically, it was Ostwald who first initiated the doubtful sentiment that equilibrium denoted a state independent of time,² a pronouncement which has probably influenced later chemical ideas much more than Ostwald had intended. Ostwald's idea of dynamic equilibrium embodied the concept of a balance of forces, a state where actions and reactions were equal and opposite. It is therefore a misleading concept to identify equilibrium as a timeless chemical process; the state of molecules at some instant A cannot be identical with the equilibrium state at instant B. The concept of dynamic chemical equilibrium also embodies the concept of change, which is synonymous with time.

1. W. Ostwald, L'Evolution d'une Science, La Chimie. Paris, 1909, 267.

2. W. Ostwald, Faraday Lecture, Chem. Soc. J., 1904, 85, 509

Theobald believes that the sense of time in chemistry is different from its sense in physics, and more akin to its sense in the life sciences - 'an equilibrium sense of time, rather than a dynamic and Newtonian sense'.¹ Yet we have seen in the present work, that it was undoubtedly necessary for chemists to accept and explore the dynamic nature of rate processes before chemical kinetics could emerge. Both Guldberg/Waage and Harcourt/Esson applied the principles of the dynamic balance of forces to form analogies for chemical rate processes.

This apparent paradox, the concept of ceaseless motion amidst seeming rest, was, curiously, totally acceptable to chemists of the nineteenth century. We have seen how Edmund J. Mills expressed his views on the matter.² And Mendeléeff, addressing an audience at the Royal Institution in 1889, attempted to apply to chemistry, 'one of the Principles of Newton's Philosophy'.³ In any chemical system, from the stars to the minutest atoms, Mendeléeff discerned,

1. D.W. Theobald, private communication, 1978.

2. See this work, Part 2, Matter, Motion, Change and Continuity.

3. D. Mendeléeff, 'An Attempt to apply to Chemistry one of the Principles of Newton's Natural Philosophy'. 1889, Reprinted in The Royal Institution Library of Science, Physical Sciences, Vol. 3, Ed. by W.L. Bragg, G. Porter, Elsevier, 1970, 540.

a harmonious order which is commonly mistaken for complete rest, but which is really a consequence of the conservation of that dynamic equilibrium which was first discerned by the genius of Newton,--namely relative immovability in the midst of universal and active movement.¹

The concept of static Nature in perpetual motion was, of-course, a familiar one.² In the Periodic Laws, Mendeléeff saw an analogy to those annual or diurnal changes with which we are so familiar on earth. Days and years follow each other: 'but, as they do so, many things change; and in like manner, chemical evolutions, changes in the masses of the elements, permit of much remaining undisturbed, though many properties undergo alteration. The system is maintained according to the laws of conservation in nature, but the motions are altered in consequence of the change of parts', he wrote.³

Mendeléeff thus reconciled the conflicts of chemical rest and motion by philosophical analogy with the laws of Nature, typifying the approach of the Natural Philosopher. Because chemical combinations

1. D. Mendeléeff, ibid. , 541.

2. For a nineteenth century view of motion see T. Merz, A History of European Thought in the Nineteenth Century, New York, 1965, Vol. 2.

3. D. Mendeléeff, op. cit., 558

took place with so much ease and rapidity, possessed so many special characteristics, and were so numerous, their simplicity and order were hidden from investigators.¹

But Mendeléeff considered, in his day, that man had discovered and was continuing every hour to discover what remained unchanged in chemical evolution, and how changes took place in combinations of the unchangeable.²

Just as the meaning of chemistry has changed from time to time, so it appears, had chemistry's ultimate aim. Like Mendeléeff, Lothar Meyer, writing in 1888, considered that 'the period has arrived when the investigation of the why and the wherefore of the formation of new compounds will be the chief object of research, instead of the mere attempt to prepare such bodies.'³ But by the early years of the present century, chemists like J.W. Mellor for instance, had come to believe that chemical philosophy related strictly to the question how and not why: 'And this is the purpose of chemical science,' wrote Mellor,

to describe in the simplest possible manner the phenomena associated with matter in the act of changing. The more important advances of modern

1. Mendeleeff, op. cit., 541

2. ibid. , 542

3. D. Mendeléeff, op. cit. , 558

science have been achieved by keeping the descriptive, not the causal relations of phenomena constantly in view. In consequence, 'why' is rapidly disappearing from our vocabulary. 'How' is the direct object of attack. Our laws relate how, not why phenomena occur.¹

And in contemporary times, Theobald, like Mellor, holds that the "process" of 'what' constitutes a chemical activity whereas, the causal process of 'why' pertains to physics.² Yet we have seen that Meyer, writing in 1863, took a totally different premise, in that: the ultimate aim of chemistry, as a branch of the natural sciences, was to seek the causal connection of phenomena in such a way that the resulting phenomena could, in all possible cases, be predicted from the given conditions.³

In her historical study of chemical composition, Freund's approach to the inductive sciences was that there was no inherent difference between the methods employed in chemistry and physics.⁴ The philosophies of

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1. J. W. Mellor, Chemical Statics and Dynamics, London, 1904, 2.
 2. D.W. Theobald, op.cit., 204.
 3. L. Meyer, Modern Theories of Chemistry, 1862, trans. by P. Bedson, W. Williams, from the 4th Edition, 1888, xx.
 4. I. Freund, The Study of Chemical Composition, New York, 1968, Introduction, first published in 1904, Cambridge University Press.

Whewell and Jevons were, in her account, equally applicable to the two sciences.¹ In each case, the scientific method to be employed followed the sequence:

- (1) The collection of facts, which corresponds with finding an answer to the question - what happens?
- (2) The classification of these facts, and the generalisation from these classified facts, which yield the laws and which answers the question how do these things happen?
- (3) The explanation of all that has been found to occur in terms of a hypothesis devised for this purpose, which supplies an answer to the question why do these things happen? And finally the welding together of all these processes in the theory of science.²

1. Yet even in the nineteenth century controversy over differences of methods employed in chemistry and physics were in evidence. The Cambridge chemist G.D. Liveing took exception to Whewell's designation of chemistry as intrinsically an inductive science, incapable of mathematical expression; for while he (Liveing) allowed that chemistry was not yet an exact science, he felt that it would not be long before it would be possible to predict the chemical behaviour of matter by mathematical deductions from mechanical principles. He consequently applauded moves towards the study of chemical thermodynamics and welcomed text-books that viewed chemistry as a system of principles rather than a set of phenomena: G.D. Liveing, Presidential Address to Section B, B.A.A.S. Reports, 1883, p. 479. See G.K. Roberts, The Liberally Educated Chemist, Chemistry in the Cambridge Sciences Tripos, 1850-1914, to be published in Historical Studies of the Physical Sciences, Vol. 11, 1980, in press.

2. I. Freund, op cit. ,30.

Freund pointed out the difficulties of distinguishing between the processes described by (2) and (3) above, and concluded that science was perhaps, as yet, unable to answer truly the question why, only how.¹

1. I. Freund, op cit. ., 30.

(b) The Role of Methodology

Even allowing for the fact that a fine differentiation between the ultimate why's and how's of chemistry and physics relate to semantics rather than philosophy, the problem of finding a common philosophical basis for chemistry within the physical sciences remains. It is difficult, to see, for instance, how an episode in the history of chemistry, as exemplified by the present study on the development of temporal concepts, can fit comfortably into any of the current theories in the philosophy of science. According to Lakatos:

the great scientific achievements are research programmes which can be evaluated in terms of progressive and degenerating problem-shifts; and scientific revolutions consist of one research programme superseding (overtaking in progress) another.¹

And further more that:

A research programme is said to be progressing as long as it's theoretical growth anticipates its empirical growth, that is, as long as it keeps predicting novel facts with some success; it is stagnating if its theoretical growth lags behind its empirical growth, that is

1. Method and Appraisal in the Physical Sciences.
The Critical Background to Modern Science, 1800-1905
Ed. by C. Howson, Cambridge, 1976, 9.

as long as it gives only post-hoc explanations either of chance discoveries or of facts anticipated by, and discovered in, a rival programme.¹

The establishment of methods for observing the course of chemical change may, for example, be thought to constitute just such an achievement. Yet it is doubtful whether any of the developments leading to it can be said to have followed any single methodology. The evaluation of time factors in chemistry was an important part of chemical progress in the nineteenth century. But, as we have seen, the rate of chemical change and related ideas were to evolve and to become incorporated into chemical theory by the slow accumulation of empirical data, rather than by any simple revolutionary discovery superseding a previous one. For chemistry, no such previous time concept existed. The temporal concepts of alchemy were not the precursors of chemical dynamics. Indeed, there is some truth in the belief that the philosophy of chemistry should not be confused with that of alchemy.²

The lack of correlation between the methodologies

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1. Howson, *op. cit.* p. 11. For reviews of Lakatos' methodology of scientific research programmes, see Brit. J. Hist. Sci., 1979, 12, 301-314.
 2. Theobald, for instance believes that chemistry is not the child of alchemy, which was 'not replaced by anything', but declined naturally. See D.W. Theobald, op. cit., 205.

described, for example, by Lakatos, (typifying many other schools of thought described in the same volume) and the apparent path of developments described in this present study, is all the more perturbing when it is recognised that there is a distinction between what scientists are supposed to do, and what is done in reality; a distinction between 'appraisal in science and appraisal in the history of science.'¹ Lakatos' arguments were primarily addressed to the philosophers of science and: 'aims at showing how he can - and should - learn from the history of science. But the same arguments also imply that the historian of science must, in turn, pay serious attention to the philosophy of science and decide upon which methodology he will base his internal history.'²

A clue to this 'chemical' dilemma may perhaps lie in the fact that some philosophers of science have a tendency to exclude completely from their 'methodologies' the ambient human, social and environmental factors

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1. J. Lakatos, in Method and Appraisal, op. cit.
 2. ibid. p. 36. The problem of methodology in the history of science has been frequently discussed. As Mary Hesse put it 'The historiography of science, more than the history of other aspects of human thought, is peculiarly subject to philosophic fashion': Reasons and Evaluation in the History of Science, in Changing Perspectives in the History of Science, Essays in Honour of Joseph Needham, C.U.P. 1974, p. 127; see also M. Hesse, Internal and External Causation of Scientific Ideas, in Human Implications of Scientific Advance, Proceedings of the Fifteenth International Congress of the History of Science, ed. by E. G. Forbes, Edinburgh, 1978; S.R. Mikulinsky, Internalism - Externalism, Controversy as a Phony Problem, ibid, 88

in which the scientist worked and made 'discoveries'. This, of course, is the nature of philosophy. But unlike pure metaphysical thought, philosophy of science, and chemical science in particular, cannot occur in the abstract nor be divorced totally from the realities of the time. What comprises an element in 'methodology' may turn out to be no more than a factor of circumstance. The work of Alexander Williamson, which has been discussed earlier, may serve as an illustration. His work on the synthesis of ethers in 1850-55, not only provided a new chemical 'method', but also provided an explanation for the 'mechanism' by which the reaction occurred.¹

Williamson introduced the concept of time and the term 'velocity' in relation to chemical processes and was the first to give a dynamic interpretation to the idea of chemical equilibria.² This same work also provided evidence which helped decide the issue between the 'radical' and 'type' theories, then prevalent. All in all, therefore, Williamson's work contained sufficient 'achievements' to conform to Lakatos' definition of 'scientific revolution'. Williamson himself was aware of this aspect of his

1. Report of the Twentieth Meeting of Brit. Ass. for Adv. of Science, 1850, 2, 65.

2. Papers on Etherification and on the Constitution of Salts by A.W. Williamson (1850-1856), Alembic Club Reprints, No. 16, Edinburgh.

work when he wrote:

Innovations in science frequently gain ground only by displacing the conceptions which preceded them, and which served more or less directly as their foundation.

Williamson did not see his new ideas as 'revolutionary', rather as a case of scientific reconciliation. He continued:

But, if the view which I have here presented be considered a step in our understanding of the subject, I must beg leave to disclaim for it the title of innovation; for my conclusion consists in establishing the connexion and showing the compatibility of views which have hitherto been considered contrary.¹

Despite the revolutionary nature of this 'research programme', the results were not to become accepted into the general corpus of chemical theory until after a long interval of time had elapsed. It cannot be said to have been embraced (either then or later) as a new element of 'progressive problem shifts', except perhaps as a new mode of chemical synthesis. As we have seen, the final establishment of reaction velocity as a chemical concept came eventually from divergent

1. A. W. Williamson, Phil . Mag., 1850, 37, 354

quarters and arose from a different approach. The acceptance of a theory - whether by overturning of another (as in the case of phlogiston theory¹) or the introduction of entirely new criteria - thus face very different paths and problems at different times. The process of this 'acceptance', it would seem, is never simple nor straight forward and it is difficult to see how such diversity can be contained in any one of the 'methodologies' of science.²

These arguments, though they do not help to answer the original question as to why there has been so little development in the philosophy of chemistry, do indicate some of the difficulties to be faced. Returning to the fundamental question of what chemistry constitutes and what its final aims are, Theobald, in considering philosophy in chemistry, has put forward a recent view:

In chemistry we are often setting out to understand what has actually occurred rather than deliberately contriving to fulfil predictions. We are, so it has been said, telling 'likely stories' rather than hazarding and testing prophecies.³

1. Method and Appraisal in the Physical Sciences, op. cit., 181.

2. ibid. p. 1. Lakatos lists these as: Inductivism, Conventionalism, Methodological Falsificationism, Methodology of Scientific Research Programmes, Internal and External History.

3. D.W. Theobald, op. cit., 209.

This modern interpretation of the aims of chemistry rather implies that predictive theories are totally uncharacteristic of chemistry, but are typical of physics.¹ But eminent examples of chemical 'predictions' can be found, such as Mendelēeff's prediction of 'unknown' elements in the Periodic Table. He clearly saw a predictive role for chemistry when he commented 'Man has learned to predict, not only what possible combinations may take place, but also the very existence of atoms of unknown elementary bodies'²

Theories and laws have had different functions in the historical development of physics and chemistry.³ Caldin has discussed the relation between laws and theories in the structure of chemistry.⁴ Taking the atomic theory as an example, Caldin wrote:

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1. Theobald, op. cit., 213.
 2. D. Mendelēef, 'An attempt to apply to Chemistry one of Principles of Newton's Natural Philosophy'; 1889, in: The Royal Inst. Lib. of Sci. Series, Physical Sci., ed. W.L. Bragg, G. Porter, London, 1970, Vol. 3, p. 542.
 3. See for example Meyerson, op. cit., 17.
 4. E.F. Caldin, The Structure of Chemistry in Relation to the Philosophy of Science, 1961, London, 17, 25.

Dalton invented the theory with the aid of his imagination, as an interpretation of certain observations, and adjusted it until a variety of its consequences agreed with known laws. The theory is a construction, not a deduction. It goes beyond representing the laws; it interprets them.¹

This element of invention in establishing scientific theories in the inductive sciences was recognised by Whewell long ago when he said that, to discover a conception of the mind, which would justly represent a train of observed facts was, in some measure, a process of conjecture --- 'and the business of conjecture is commonly conducted by calling up before our minds several suppositions --- he who has to discover the laws of nature may have to invent many suppositions before he hits upon the right one'.² In chemical activities, as Caldin points out, theories are of interest because they offer explanations of observations that would otherwise be puzzling. They are developed to help us understand phenomena, not merely to describe them.³ Furthermore, explanations of unfamiliar laws of chemistry, have, not infrequently required an analogy with familiar, mechanical, models. Mellor, in his Chemical Statics and Dynamics certainly advocated this

1. Caldin, op. cit., 28.

2. W. Whewell, Philosophy of the Inductive Sciences Cambridge, 2nd Ed., 1847, Vol.2, 54.

3. Caldin, op. cit., 32.

approach. In his view, a phenomenon could only be explained by showing how it resembled something already known. The scientific generalization explained the operations of nature by showing the elements of sameness in what, at first sight, appears to be a confused jumble of phenomena. 'Generalization is the golden thread which binds many facts together in one simple description', wrote Mellor.¹ Mellor was perhaps expressing the views of a discipline for which the art of establishing laws and theories was still a relatively new one. The 'simple description' seldom proved to be so simple. As Caldin also pointed out, explanation does not always depend on familiarity.² More often explanations or theories in chemistry are attempts to formulate statements about nature, by conjecturing or interpreting the evidence presented by natural phenomena.³

Developments in chemical methodology may therefore be described as constituting approximations. For, however well chosen the model, it cannot be taken as an exact description of reality, and at best, can only be regarded as providing analogies; such paradigms necessarily embrace an element of uncertainty and incompleteness. However, unless this inherent uncertainty

1. J. Mellor, Chemical Statics and Dynamics, 1904, London, .2.

2. Caldin, op. cit., 34

3. In physics, the procedure, it has been remarked, may arise from a totally different premise i.e. physicists have frequently had difficulties in finding sufficient observations to prove their theory; see Theobald, op. cit.

is recognised and accepted, theories, which may in fact be quite valid, or partially so, are liable to suffer untimely death or rejection. The history of theories in chemical affinity offers perhaps an apposite example of this. Based as they were, originally, on Newtonian mechanics, they suffered a fate which could not be redeemed, because the Newtonian models, however attractive, could only approximate to chemical reality.

The failure of familiar analogies to account completely for chemical phenomena, in fact produced far-reaching consequences in the attitudes which chemists were forced to assume in developing their subject. It was safer, after all, to concentrate on practical chemical preparations than to indulge in uncertain theories. Meyer, for instance, recalled that Berthollet was the first to subject the influence of the mass of reacting substances to a rigorous scientific examination.¹ His attempts to explain this influence mathematically, however, assumed erroneous models, as a result of which his theories were discredited.² Significantly, Meyer believes that it was a direct consequence of chemists accepting the Atomic Theory that helped to sever the links between chemistry and physics, a link which Berthollet had sought to strengthen by applying the laws of mechanics to chemical phenomena. As a consequence of this new matter theory the attention of chemists became riveted

1. L. Meyer, op. cit., XXIII

2. ibid.

to the preparation, study and classification of an enormous number of new compounds, predicted by the atomic hypothesis. Chemistry thus became more and more a descriptive natural science, neglecting the general theoretical speculations advocated by Berthollet. Meyer, in fact, gives us an extremely interesting clue as to why nineteenth century chemists were proceeding in the manner that the history of the subject now records. The process of development in chemistry has been such that each theoretical view could only be deduced from a large, and often widely distributed, number of facts. Meyer wrote:

Hence arose the feeling of uncertainty or doubt as to the value of theoretical considerations generally, which frequently led to speculations concerning the origin and nature of phenomena being incidentally announced, and even in some cases, not expressed but left to the reader to deduce.¹

The result was that chemists of the day developed great caution and reluctance, even in formulating general theories. The opposition to the recognition of theories was extremely strong; many of the theories later accepted had first, as history shows, to battle in

1. L. Meyer, Modern Theories of Chemistry, 1864, trans. by P. Bedson, W. C. Williams, London, from the fifth Edition, 1888, XXX.

vain. Berry, for instance attributes the antagonism of many chemists to Avogadro's hypothesis to this streak of chemical over-caution.¹

Thus, the degree of uncertainty inherent in scientific laws and hypothesis, may have been transferred by chemists, from the innate nature of laws and theories themselves, to the practise of not trusting in theoretical speculations at all. Meyer, as we have seen, hinted as much about chemical developments in his own day, as indeed did Williamson. This cautious attitude by chemists to their subject may go a long way in explaining the order of scientific developments as viewed in historical perspective.

And as in all historical retrospection, it allows us, with the wisdom of hind-sight, to say that systematization and ordering of phenomenological data into principles is only a first, but not sufficient, criterion for scientific progress. The discovery by chemists of the need for this systematization thus amounted only to the means to an end, rather than the end itself. Yet this knowledge permits us a very different approach from that commonly held by chemists, both of the nineteenth century and in contemporary times,²

1. A.J. Berry, Modern Chemistry, Cambridge, 1946, p. 222.

2. As recently as 1978, Erwin Chagraff has described chemistry as 'that most real of exact sciences' see Heracleitean Fire - Sketches from a Life before Nature, Rockefeller University Press, 1978.

who saw and continue to see the establishment of chemical laws and theories as giving an 'absoluteness' or 'exactness' to their subject. We have already mentioned such views expressed by chemists like Freund and Mellor, whose chemistry text-books had considerable influence.¹

And Berry, writing in 1946, considered that:

one of the most distinctive features of the development of chemistry has been its gradual transformation from a largely descriptive science into an 'exact' one. The emphasis has been very markedly in the direction of what might be termed kinetic chemistry.

This process, in which much of the methodology of chemistry has approached more closely to that of physics, has been necessarily accompanied with a greatly increased importance of the theoretical aspects of the science.²

This view can be seen to echo closely the views held by a large number of nineteenth century chemists.

In retrospect, however, this view was somewhat

1. M.M. Pattison Muir believed that Freund's work was to be classed among the really great works of chemical literature.

2. A.J. Berry, Modern Chemistry, 1946, Cambridge, 221.

premature. For chemistry, explanations cannot be said to have completely fulfilled, yet, the criteria for scientific laws, attributed by Meyerson to Berkeley for example.

For the laws of nature being once ascertained, it remains for the philosopher to show that each thing necessarily follows in conformity with these laws, that is, that every phenomenon necessarily results from these principles. This is to explain the phenomena; that is, to assign the reason why they take place.¹

The philosophy of physics has developed largely on the assumption of the absolute truth of causality. Thus, Cournot believed that every time we dealt with phenomena of the physical order, if these phenomena appear in the first place to depend on forces or causes which vary with time, it was inherent in the nature of our minds not to regard the phenomenon as accounted for until it had been brought back to depend on permanent causes, immutable in time.²

Meyerson's ultimate view of the physicists' approach

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1. E. Meyerson, Identity and Reality, op. cit., Chap. 1
 2. Traité de l'Enchaînement, Paris, 1861, 276.

to physical laws and causality is this desire 'to make laws immutable in time'. In his view, science, in general, does not treat things¹ and laws in the same way in relation to time.² 'Variation of the object in time is what it must study in the first place, and the most natural form of the law is that which indicates the evolution of the phenomenon as a function of the time as an independent variable.'³ In Meyerson's picture of physical reality, what remains eternally constant is the relation between the change in phenomenon, and time, because time, in its essence, flows always and uniformly in the same direction.⁴

To a large extent, this somewhat historical approach to physical causality has been superceded by developments in the present century. The principle of uncertainty is now accepted as a vital element of scientific progress.⁵ In chemistry, we may say that the incorporation of time elements into reaction processes was only the first approximation of the 'variation of the object in time'. But as yet, exploration of this part of chemistry has hardly begun.

1. Presumably, this refers to anything not already law.

2. E. Meyerson, op. cit., 220.

3. E. Meyerson, op. cit., 220.

4. ibid.

5. Max Planck has discussed the dual role of uncertainty and of laws in physical theory. 'It is obvious that in an exact science, such words as certain and sure must be used with caution -- when considering the laws of physics, or indeed, any observed law, either dynamical or statistical, we are compelled by theory and experiment alike to make a fundamental difference between necessity and probability'; A Survey of Physical Theory, Dover, 1960.

(c) Conclusions

It would appear that if a common philosophical basis between chemistry and the other physical sciences is to be found, it may exist in the inherent impossibility of complete certainty in its laws and theories, as we know them today. For chemistry in the last century, as a newly emerging 'exact' science, it is not difficult to understand why chemists searched so relentlessly for an absoluteness to their scientific truth, a truth which, like that in physics, had to be 'immutable in time'. In a contemporary interpretation of chemical laws, it may perhaps be imperative to first recognise that, by virtue of their empirical nature, laws are and have always been prone to change and correction, and do not attain absolute certainty. This means that laws themselves are functions of time..¹ We have already seen an example of this in our earlier discussion of the chemist's debate on Matter Theory.² Both the atomists and anti-atomists were ultimately correct in

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1. Liebig, in a philosophical digression, came very close to stating the same thing: '-- we find that at all times the opinion obtained, (and) the conceptions were in harmony with the facts, and indeed the definition always corresponded with the logical laws, but the latter are always in opposition to the earlier; what had been held to be right is found to be wrong at a later period, and thus the subsequent definitions annul the former ones, and this goes on for centuries': J. von Liebig, 'On the Development of Ideas in Natural Philosophy', Chem. News, 1867, 252.
 2. See this work, Part 2, Matter, Motion, Change and Continuity.

their analysis, as it emerged in time. In chemistry, the typical procedure lies, as Caldin put it, between the empirical and the hypothetico-deductive.¹ The aim is to define the model more precisely, to approach closer to the paradigm. It lies, still, at some intermediate level of complexity, which Theobald has also intimated. But far from being the 'timeless' phenomenon that Meyerson and others have suggested, chemical complexities are ultimately changing phenomena. One may go so far as to say that chemistry involves a dependency on temporal concepts greater than that of physics. But, unlike the old view of science, which saw progress as the successful establishment of reality, we may view chemical truth as nothing eternal but rather with 'a high degree of confidence after adequate objective self-testing and self correction,' as a recent author put it.² We may also agree with the same author that no scientific explanation so far achieved is, in the fullest sense of the word, complete.³

What is true for science in general is perhaps

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1. E.F. Caldin, op. cit., 46.
 2. G. Gaylord Simpson, Notes on the Nature of Science, Harcourt, Brace and World, 1961.
 3. ibid.

especially true of chemistry. The chemist G.N. Lewis has said "The chemist never talks about 'in the last analysis', rather he is interested 'in the next approximation'".¹ The philosophy of chemistry may indeed be found to exist at an intermediate level, between the 'empirical and hypothetico-deductive', but certainly it deserves greater consideration than it has so far received. At the very least, it calls for a re-appraisal of the specific role of chemical developments in existing scientific methodologies.

1. J. Chem. Ed., 1963, 40, 9, 445.

3.2. Summary and Suggestions for future work.

In the present work, the development of time concepts in chemical thought has been considered from a number of different starting points: the philosophical concepts of time common to the heritage of western civilization; the development of chemistry as a phenomenon embodying change; the evolution of the concept of chemical change possessing specific speed or rate and the controversy over a dynamic theory of matter which formed the fundamental background to chemical phenomenon, both in terms of its philosophy and its historical development. We have seen how the evolution of time factors in chemistry first required an awareness and understanding of related phenomena such as the course of chemical change. These developments however, form only the very embryonic stages in the study of chemical reaction rates. The pioneering studies of Guldberg and Waage, Harcourt and Esson and van't Hoff are only the beginnings of the history of exact time studies in chemistry. The quantity of literature on this and other related discoveries which have emerged from the beginning of this century to the present time, gives an indication of the degree to which chemical rate studies have become a fully integrated part of the chemical sciences. So much so, that one pioneer in the new field of flash photolysis, where measurement of micro and even smaller intervals of time in chemical reactions have been

studied, considers the history of kinetics to be no more than fifty years old.¹ But the origins of temporal aspects of chemical change are indeed much older, as we have seen in this work.

Among the related topics which await discussion are: the development of rates of reactions in the gaseous state and their role in reaction mechanisms; catalysis; the phenomenon of periodic chemical change and a detailed analysis of the concept of chemical equilibrium.

1. Professor Sir George Porter, private communication, see G. Porter, "Flash photolysis and some of its Applications" Nobel Lecture, 1967 "Quick as a Flash", Proc. Roy. Inst. 1967, 42, 196, 193; "Molecules in Micro-time" Roy. Inst. Friday Evening Discourse, 7th Dec. 1973.

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(see also the Brief Bibliography to Time on P.59)

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